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THE UNIVERSITY OF ALBERTA

SOLUBILITIES OF GASES IN HEXADECANE, TOLUENE, AND TOLUENE + BITUMEN SOLUTIONS

by

(C) HARBINDER PAL SINGH

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

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EDMONTON, ALBERTA

FALL, 1987

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(SIGNED) H. P. Singh

PERMANENT ADDRESS:

342 JHAWAR HOUSE

MODEL TOWN

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DATE: May 25, 1987

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled SOLUBILITIES OF GASES IN HEXADECANE, TOLUENE, AND TOLUENE + BITUMEN SOLUTIONS submitted by Harbinder Pal Singh in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE.

Supervisor

External Examiner

Date April 21, 1987.

Dedication

To

Smt. Premjit Kaur and Late S. Charan Singh

ABSTRACT

The solubilities of nitrogen, methane, carbon dioxide, propane, and sulfur dioxide in toluene; nitrogen, methane, ethane, propane, carbon dioxide, and sulfur dioxide in hexadecane; and methane and carbon dioxide in solutions of bitumen in toluene were determined at different pressures (0.8 to 3.0 atm) and temperatures ranging from 298 to 343 K. The measurements were carried out in a newly designed isobaric equilibrium apparatus, with a reliability of ±1%. Test measurements for oxygen dissolved in pure water showed excellent agreement with recent high-precision results. Henry's constants were evaluated from the solubility data. From these measurements the free energies, entropies, and enthalpies for the process of transferring the solute molecules from the gaseous phase into the liquid were computed. Our results show that ln ($H_{2,1}$) is linearly dependent on 1/T as expected on the basis of earlier thermodynamic investigations.

It was observed that the solubilities of carbon dioxide, sulfur dioxide, ethane, and propane decrease with rising temperature while those of nitrogen and methane increase with rising temperature. A tentative interpretation of this behavior is explained, based on the solvent density and the entropy of solution in the Henry's-law limit.

The solubility data obtained are compared to the results obtained by the Gas Liquid Chromatography (GLC) method (in this laboratory).

For highly soluble gases, the isobaric equilibrium and the GLC methods can be used for measuring the solubilities. However, for systems where $H_{2,1}$ > 100 atm, the isobaric equilibrium method is better than the GLC method. It is recognized that an accurate evaluation of the column dead time (for the GLC) is the critical factor for measuring the solubilities of less soluble gases.

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LIST OF SYMBOLS

B	2nd virial coefficient of the gas
C_p	molar isobaric heat capacity
f_2	gas phase fugacity
$H_{2,1}$	Henry's constant of solute (2) in solvent (1)
$H_{2,b}$	Henry's constant of solute (2) in bitumen solution
H_a	apparent Henry's constant
L_w	concentration [weight of bitumen / (weight of toluene + weight of bitumen)]
m_1	mass of the solvent
M_1	molecular weight of the solvent
M_2	molecular weight of the solute (gas)
n_1	number of moles of solvent in which the gas is dissolved
n_2	number of moles of solute (gas) that is dissolved
n_3	number of moles of bitumen
P_1	partial vapor pressure of solvent at temperature T
P_2	partial pressure of the gas

P_3 partial pressure of bitumen

P_m measured pressure of the system

$P_{s,1}$ vapor pressure of the pure solvent

P_1^i internal pressure of the solvent

P_2^c critical pressure of the solute (gas)

R gas constant (82.06 cm^3 atm K^{-1} mol^{-1})

T thermodynamic temperature (K)

T_b normal boiling point

T_1^c critical temperature of the solvent

T_2^c critical temperature of the solute (gas)

u ultrasonic speed

V volume of gas dissolved in solvent

V_s volume of the saturated solution

V_1° molar volume of the pure solvent

V_1^* partial molar volume of the solvent

V_2^* partial molar volume of the dissolved gas

V_{Hg} volume of mercury

V_2^∞ partial molar volume of the dissolved gas at infinite dilution. Values are given in Table 5.11

x_1	mole fraction of the solvent
x_2	mole fraction solubility of gas in liquid
x_3	mole fraction of bitumen
ΔG_2°	standard Gibbs free energy of solution
ΔH_2°	standard enthalpy of solution
ΔS_2°	standard entropy of solution
α	coefficient of expansion
β	isothermal compressibility
β_s	isentropic compressibility
δ	solubility parameter

CHAPTER 1

INTRODUCTION

The study of gas solubilities has, in addition to its profound theoretical interests, many practical applications particularly in the petroleum and petrochemical industries. The small solubility and the variety of gases available to use as probes have made the solubilities of gases in liquids an excellent tool to investigate liquid and solution structure and properties. In fact, research activities can be traced to requirements originating in surprisingly diverse areas of pure and applied sciences. For instance, chemical process design often needs reliable estimates of vapor-liquid equilibrium (VLE) for multicomponent systems containing one or more gases (non-condensables).

Other areas where gas solubility data are frequently needed are geochemistry, environmental science (pollution control), and biomedical technology. Since life cannot exist without water, studies of simple aqueous solutions, in particular of the rare gases and of hydrocarbons, have held a prominent position in biophysics.

Perhaps the most important studies on such model systems have provided information on hydrophobic effects, which are thought to be of importance in complex biological processes. Some of these are:

1. The strongly enhanced solubilities of oxygen in perfluorinated hydrocarbons (1) as compared to the solubilities in the parent hydrocarbons. These substances are chemically inert enough to be used as blood substitutes and

as gas carriers in liquid breathing (2-4).

2. Solubilities of gases in selected solvents, for instance, in long-chain alcohols (5), and their relations to anesthetic potency (6).
3. Solubilities of Freons and hydrocarbons in water (environmental pollution control) (7,8) and of oxygen and ozone in water (water treatment and waste water treatment) (9-11).
4. Some gases such as hydrogen sulfide, carbon dioxide, and sulfur dioxide are of particular interest because of the demand for removal of these "acid" gases from refinery and natural gases (12-16).
5. Solubilities of carbon dioxide, hydrogen, and other light gases in various (high molecular weight) solvents (17-20) are important for a number of engineering processes, such as hydrofining of oil and coal, enhanced oil recovery and *in-situ* bitumen recovery.
6. A knowledge of the solubilities of gases in aqueous solutions of surfactants (21,22) is important because of the ability of aqueous micellar solutions to solubilize various organic solutes which are normally very sparingly soluble in water.

The thermodynamic properties of gases in liquids are also of interest, especially for high molecular weight liquids where a significant size and weight disparity between the solute and solvent can produce unique solution properties. Good models have been developed for some hydrocarbon systems. However, many more data are needed for other gases, such as those already mentioned, as well as water, nitrogen, the nitrogen and sulfur oxides,

and the inert gases.

Solubility data are needed for other light gases that are used in extractive distillation and supercritical fluid extraction, and for initial screening and subsequent design of these processes.

There have been a number of recent reviews of various aspects of the solubilities of gases in liquids: for instance by Clever and Battino (23), Pierotti (24), Wilhelm *et al*.(25), Gerrard (26), and Wilhelm (27-29). Additional information may be found in the literature devoted to solutions of non-electrolytes in general [Wilhelm (30), Goldman (31), Ben-Naim (32), Prausnitz *et al*.(33), Van Ness and Abbott (34)].

Even though the experimental determination of gas solubilities is often difficult and time-consuming, the demand is such that a large number of these measurements have been carried out at room temperature. Collections of such data have been reviewed by Wilhelm and Battino (25,35). Unfortunately, gas solubility data are scarce for temperatures other than the standard 298 K and for solvents other than water and hydrocarbons.

The purpose of the present work is threefold:

1. To measure the solubilities of gases in different liquids and to assess the performance of the equilibrium apparatus that was designed (by Hai-ke Yan) in this laboratory.
2. To compare results obtained with the traditional equilibrium method and with the Gas Liquid Chromatography (GLC) method.
3. To obtain data pertinent to petroleum problems.

Because users of gas solubility data want such information for many different temperatures and pressures and for many different bitumens and oils, it is impractical to measure every solubility that might be needed. Instead, we try to make maximum use of a reasonable number of reliable solubility data in several ways, as follows:

1. One way is to make use of thermodynamic equations that permit very reliable interpolations and reasonably reliable extrapolations to different pressures and temperatures than those which have been directly investigated in the laboratory.
2. Another complementary approach is to develop and make use of predictive theories which are mostly based on combination of thermodynamics with equations of state, but potentially based more directly on statistical mechanical molecular theories. These theories require experimental data to permit assessment of the reliability of the proposed model and also to permit evaluation of one or more empirical parameters that have always been needed in such treatments.
3. There is also a need for a soundly based method of dealing with and making full use of experimental results obtained for mixtures, such as bitumen + diluent.

There is another need for thermodynamic analysis and correlations or predictions based on equations of state. It is generally known that **apparently** good measurements sometimes lead to incorrect results; such experimental errors are most common when one works with difficult systems. Although

reliable measurements of solubilities of gases in low-volatility liquids having low viscosities have been made in several laboratories (including the present work), similar measurements on very viscous bitumen and heavy oils are more difficult and the results are therefore less well established as being truly reliable. Moreover, neither clever data treatment nor semi-theoretical predictive methods can ever provide a substitute for reliable and accurate measurements. At the most, such computational methods can help in distinguishing between the most reliable experimental results and those which are less reliable. We need every device we can develop that will help us test the reliability of our experimental results and also results from other laboratories, because of the difficulties associated with making gas solubility measurements with bitumen and heavy oils.

Another reason for being interested in thermodynamic analysis of solubilities of gases in bitumen and oils is because of the thermal effects associated with dissolving gases in bitumen/oils as would occur during the *in situ* recovery of bitumen. Although it is possible (at least in principle) to measure such thermal effects calorimetrically, previous experience in several laboratories has demonstrated that such measurements are very difficult and require complicated equipment for liquids having high viscosities. However, it is not impossible to obtain information about these thermal effects because the desired enthalpy (heat) changes can be calculated reliably by means of equations of classical thermodynamics, provided that one has the correct equilibrium solubility data.

CHAPTER 2

THERMODYNAMICS OF GAS-LIQUID EQUILIBRIUM

2.1 Basic Thermodynamic Considerations

When discussing equilibrium of phases containing more than one component, it is frequently convenient to distinguish between a mixture and a solution. In a mixture all components are on equal footing; thermodynamically they are all treated in the same manner, that is to say symmetrically. On the other hand in a solution (often dilute), one (or several) of the components is/are present in excess and is/are called the solvent or mixed solvent, while the remaining component(s) at low mole fraction(s) is/are classified as solute(s). In general, the thermodynamic treatment of dilute solutions is often asymmetric in that solute and solvent are treated differently. There is nothing fundamental in this distinction between a dilute solution and a mixture, and although not always stated explicitly, thermodynamic analysis of gas-solvent systems proceeds along the same lines as for other phase equilibrium problems. A survey of the literature reveals that there are several monographs (26,34,36,37) and review articles (25,27,28,29,39-41) concerning the thermodynamics of gas-liquid equilibrium, mostly from the point of view of dilute solutions.

Consider a PVT system with uniform temperature T and pressure P, containing component 1 (the solvent) and component 2 (the solute) in both the vapor or gas (g) phase and the liquid (ℓ) phase. Thermodynamic equilibrium is characterized by the equality of the chemical potentials, for each component i,

in the co-existing phases:

$$\mu_i^g = \mu_i^\ell \qquad [2.1]$$

Connection with the observable variables, total pressure P, mole fraction composition y_i of gas and x_i of liquid, respectively, is usually established with the aid of the two auxiliary functions : the gas-phase fugacity coefficients Φ_i and the liquid phase activity coefficients γ_i. The equations are

$$\mu_i^g (P,T,y_i) = \mu_i^{*g} (T) + RT \ln P + RT \ln y_i + RT \ln \Phi_i$$

$$= \mu_i^{*g} (T) + RT \ln f_i \qquad [2.2]$$

and

$$\mu_i^\ell (P,T,x_i) = \mu_i^{o\ell} (P,T) + RT \ln x_i + RT \ln \gamma_i$$

$$= \mu_i^{o\ell} (P,T) + RT \ln a_i \qquad [2.3]$$

where $f_i = (P\, y_i\, \Phi_i)$ is the gas phase fugacity

$a_i = (x_i\, \gamma_i)$ is the liquid phase activity

$\mu_i^{*g} (T)$ is the chemical potential (depends only on the temperature) of component i in the gas phase

$\mu_i^{o\ell} (P,T)$ is the chemical potential (depends on both temperature and pressure) of component i in the liquid phase.

For the *gas phase*, the standard state is generally the ideal gas state at the specified temperature and at P = 1 atm. For the *liquid phase* of solutions of gases (where the pure component "gas" is often supercritical), most frequently the so-called unsymmetric convention for activity coefficients is adopted.

Thus for a binary system :

for solvent (i = 1) : $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$

for solute (i = 2) : $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 0$

The standard state chemical potential of the subcritical component (solvent) is the chemical potential of the pure liquid at system temperature and pressure. On the other hand the activity coefficient of the solute is taken as approaching unity at infinite dilution. Hence $\mu_2^{\circ \ell}$ can be interpreted as the chemical potential of pure solute in a hypothetical liquid state corresponding to extrapolation from infinite dilution (which serves as reference state) to $x_2 = 1$ along a line where $\gamma_2 = 1$, that is, along the Henry's law line.

Substitution from Eq. [2.2] and [2.3] into Eq. [2.1] and rearrangement gives

$$\Phi_2 y_2 P / \gamma_2 x_2 = f_2 / \gamma_2 x_2 = H_{2,1} \qquad [2.4]$$

$$H_{2,1} = \exp [\Delta \mu_2^{\circ} / RT] \qquad [2.5]$$

where $\Delta \mu_2^{\circ}(P,T) = \mu_2^{\circ \ell} - \mu_2^{*g}$ is the standard change of the partial molar Gibbs energy upon solution. $H_{2,1}$ is called the Henry's constant of substance 2

in solvent 1.

The value of the Henry's constant depends strongly on the nature of the solvent, the gas and the temperature. This well-defined and experimentally accessible quantity may be evaluated (at the saturation pressure of the solvent, $P_{s,1}$) from a plot of (f_2 / x_2) versus x_2 by extrapolating to $x_2 = 0$:

$$\lim_{x_2 \to 0} (f_2 / x_2) = H_{2,1} \qquad [2.6]$$

The pressure dependence of Henry's constant is negligible at low pressures, but must be considered at high pressures.

Since

$$(\partial \ln H_{2,1} / \partial P)_T = V_2^{\infty}$$

and hence

$$\ln H_{2,1} = \ln H_{2,1}(P_{s,1},T) + \int_{P_{s,1}}^{P} (V_2^{\infty} / RT)\, dP$$

$$\cong \ln H_{2,1}(P_{s,1},T) + [V_2^{\infty} (P - P_{s,1})] / RT \qquad [2.7]$$

If the solution temperature is well below the critical temperature of the solvent, then as a first approximation V_2^{∞} (partial molar volume of component 2 at infinite dilution) is assumed to be independent of pressure (42-45).

$H_{2,1}(P_{s,1},T)$ is Henry's constant evaluated at an arbitrary pressure $P_{s,1}$.

Equation [2.7] is called the Krichevsky-Kasarnovsky (46) equation. This equation is accurate for representing the solubilities of sparingly soluble gases

up to high pressures. A graph of ln $H_{2,1}$ versus P (P is in general much greater than $P_{s,1}$) yields $H_{2,1}$ ($P_{s,1}$,T) from the intercept and V_2^{∞} from the slope. The latter is generally in good agreement with experimental values which can be obtained from density measurements. The Krichevsky-Kasarnovsky equation holds in general for small values of x_2 and temperatures far removed from the critical temperature of the solution.

2.2 Calculations

Gas solubilities have been expressed in many ways. The more popular of these along with interconversion formulae are given in the review by Battino and Clever (40). In this work the gas solubilities have been expressed in terms of the mole fraction (x_2) and Henry's constant ($H_{2,1}$).

The mole fraction solubility (x_2) is defined as the ratio of the number of moles of gas dissolved to the total number of moles of both the dissolved gas and the absorbing solvent :

$$x_2 = n_2 / (n_1+n_2) \qquad [2.8]$$

where n_2 is obtained using the virial equation of state [2.9], truncated to two terms (for low-pressure experiments, where P < 0.3 MPa or 3 atm), since the variables T and P are the ones usually controlled and measured in the solubility experiments (47):

$$P_2V = n_2RT + n_2BP_2 \qquad [2.9]$$

where

$$V = V_s \pm V_{Hg} \qquad [2.10]$$

The volume V_s of the saturated solution is given by the following approximate relation:

$$V_s = n_1 V_1^* + n_2 V_2^*$$

$$\approx n_1 V_1^\circ + n_2 V_2^\infty \qquad [2.10a]$$

V_{Hg} is the volume of mercury taken out of or added to the system from the mercury bottle (for explanation see the experimental section). The plus and minus signs depend on the Ostwald coefficient of the gas, which can be either greater or less than unity.

As a first approximation, V_2^∞ can be set equal to zero, and a value of V can be computed from Eq. [2.10]. From this approximate value of V thus obtained, n_2 can be evaluated from Eq. [2.9]. A better value of V is then obtained from Eq. [2.10] and [2.10a] using a known value of V_2^∞ from the literature (48).

Note: The V_2^∞ values were calculated from an empirical correlation based on a modification of a model proposed by Smith and Walkley (49). The equation (48) used is:

$$V_2^\infty P_2^c / RT_2^c = 0.092 + 2.674\, T P_2^c / T_2^c P_1^i \qquad [2.11]$$

where P_1^i is the internal pressure of the solvent (50). For hexadecane, the value of P_1^i was calculated from the coefficient of thermal expansion and the isothermal compressibility reported by Benson and Handa (51). Details of these calculations are shown in Appendix B. The available data indicate that Eq. [2.11] will predict V_2^∞ (T, $P_{s,1}$) of any gas in any solvent to within 10%, provided the temperature is well below T_1^c. It was also assumed that the partial molar volume at infinite dilution (V_2^∞) is independent of temperature and pressure. The second virial coefficient (B) values for gases were taken from the literature (52).

Since the experiment was performed by the " wet method " in which the gas of interest is saturated with the solvent, the gas partial pressure is given by

$$P_2 = P_m - P_1 \qquad [2.12]$$

where

$$P_m = P_{\text{Heise gauge}} + P_{atm}$$

Note: $P_{\text{Heise gauge}}$ is the pressure of the gas in the solubility apparatus measured with Heise pressure gauge and P_{atm} is the atmospheric pressure recorded from a barometer.

For non-volatile solvents (e.g. hexadecane) the vapor pressure of the solvent is neglected ($P_1 = 0$) so that

$$P_2 = P_m \text{ (for non-volatile solvent)} \qquad [2.13]$$

However, when the gas solubility is appreciable and the solvent is relatively volatile, the equilibrium partial pressure of the solvent can no longer be considered to be simply the vapor pressure of the pure solvent. Here we assume that Raoult's Law ($P_1 = x_1 P_{s,1}$) can be applied to the solvent in the solution and the gas partial pressure is then

$$P_2 = P_m - x_1 P_{s,1}$$

or

$$P_2 = P_m - P_{s,1}(1 - x_2) \qquad [2.14]$$

Substituting Eqs. [2.9], [2.10], [2.11], or [2.12], into Eq. [2.8] gives

$$x_2 = \frac{P_2 [(V_s + n_2 V_2^{\infty}) \pm V_{Hg}] / (RT + BP_2)}{(m_1/M_1) + \{P_2 [(V_s + n_2 V_2^{\infty}) \pm V_{Hg}] / (RT + BP_2)\}} \qquad [2.15]$$

As a first approximation, x_2 is set equal to zero, and a value of P_2 can be computed from Eq. [2.12], which is used to obtain a value of x_2 from [2.15]. This approximate value of x_2 is then substituted into Eq. [2.12] to get a new value of P_2 and hence a new value of x_2. This process of calculating P_2 and x_2 is repeated until there is no change in the final values, and is thereby referred to as the " Iterative Procedure ". For gases in toluene the mole fraction solubilities, x_2, were calculated through an iterative procedure using Eq. [2.12] in

conjunction with Eq. [2.15].

2.3 Evaluation of P_2 for Toluene + Bitumen Solutions

For the case of a liquid (solvent) consisting of a mixture or solution of two or more well-characterized substances, the mole fraction equation may be written as :

$$1 = x_1 + x_2 + x_3 \qquad [2.16]$$

As a first approximation, we consider the mole fraction of the dissolved gas (x_2) to be equal to zero. Therefore x_1 can be calculated directly from the weights (that is $x_1 = n_1 / \{n_1+n_3\}$).

The measured pressure can be defined as

$$P_m = P_1 + P_2 + P_3 \qquad [2.17]$$

Initially, the pressure of bitumen (P_3) is taken to be equal to zero ($P_3 = 0$). So we now have

$$P_2 = P_m - P_1$$

or

$$P_2 = P_m - x_1 P_{s,1} \qquad [2.18]$$

This value of P_2 was used to calculate the mole fraction of the dissolved gas (x_2).

As a second approximation, x_1 can no longer be calculated directly from the weights due to x_2 being no longer equal to zero ($x_2 \neq 0$). Therefore, one must use the equation

$$x_1 = n_1 / (n_1 + n_2 + n_3) \qquad [2.19]$$

where n_3 is the number of moles of bitumen.

Note: Use of the mole fraction solubility requires that we know (or assume) the molecular weight of each component. We have used the molecular weight of bitumen that is derived from some independent measurements-most commonly from vapor-phase osmometry (VPO). Any molecular weight obtained in this way or in similar ways includes an overall experimental uncertainty of at least one percent. Further, it is noted that this is an average molecular weight for all of the constituents of the bitumen. From the analysis of bitumen (provided to us), the average molecular weight of bitumen ranges from 540 to 600 g/mol (see section 4.3) and we have used 560 g/mol as the molecular weight of the bitumen in our calculations.

The computed value of P_2 from the first approximation was used to calculate a value for n_2. This approximate value of n_2 was then used in Eq. [2.19] for a second approximation to get a new value for x_1, which was used in Eq. [2.18] to obtain a new value for P_2 and n_2 (from Eq. [2.9]). This new value of P_2 and n_2 was used to calculate the final value of x_2.

2.4 Henry's constant ($H_{2,1}$)

The equation for a gas in equilibrium with a solution may be written as

Gas (hyp. 1 atm, T) = Solute (hyp. $x_2 = 1$, T)

Henry's law is strictly applicable only in the extrapolation to infinite dilution; that is,

$$\lim_{x_2 \to 0} (P_2 / x_2) \approx \lim_{x_2 \to 0} (f_2 / x_2) = H_{2,1} \qquad [2.20]$$

Assuming an ideal gas phase and replacing the fugacity f_2 by the partial pressure P_2 of solute may often yield satisfactory results, provided P_2 is small ($P_2 < 1$ atm), the solubility of gas in the liquid is sufficiently low ($x_2 < 10^{-3}$), and the temperature is well below the critical temperature of the solvent. Under these circumstances, the solution may be regarded as being effectively infinitely dilute. At about atmospheric pressure for most gases equating f_2 with P_2 involves negligible errors in gas solubility measurements. For dilute solutions, where Henry's law is applicable, the following relations hold:

$$H_{2,1} = P_2 / x_2 \ (P_2) = 1 / x_2 \ (P_2 = 1) \qquad [2.21]$$

Although many gas solubility systems may obey Henry's law in this form, others do not obey Henry's law under these conditions. A simple test (53) is to put the equation in the form

$$\ln P_2 = \ln H_{2,1} + \ln x_2 \qquad [2.22]$$

If Henry's law is obeyed, a plot of $\ln P_2$ versus $\ln x_2$ will be linear and of unit

slope.

For gases that deviate from Henry's law at high pressures and large solubilities the following form of Henry's law equation was used

$$P_2 = H_{2,1}\, x_2 + H_a\, (x_2)^2 \qquad [2.23]$$

where $H_{2,1}$ is obtained by extrapolating to $x_2 = 0$ on a plot of P_2 / x_2 versus x_2.

2.5 Data Representation by Henry 's Constant

Henry's constant as a function of temperature can be correlated by two different methods due to Clarke and Glew (54) and to Benson and Krause (55, 56). These authors assume that ln ($H_{2,1}$/ atm) and its derivatives are well-behaved functions of either the thermodynamic temperature T, or the inverse temperature T^{-1}.

When adopting the former procedure (CG), the temperature dependence of $H_{2,1}$ is represented by

$$\ln [\, H_{2,1} / \text{atm}\,] = A_0 + A_1\, T^{-1} + A_2 \ln T + A_3\, T + A_4\, T^2 + \text{-----} \qquad [2.24]$$

and when adopting the Benson and Krause method, the temperature dependence of $H_{2,1}$ is represented by

$$\ln [H_{2,1} / \text{atm}] = B_0 + B_1/T + B_2/T^2 + B_3/T^3 + \text{------} \qquad [2.25]$$

where A's and B's are the constants in the equation and T is the

thermodynamic temperature. It is noted here that Eq. [2.24] when truncated to three terms is the well-known Valentiner equation (57).

Benson and Krause (56) found that a simple three-term series in 1/T fit the data well. The BK power series in T^{-1} has been much used (27,55,56,58,59,60) for representing the variation of $H_{2,1}$ with T.

For systems studied here, the standard state of the gas in the vapor phase at any temperature is defined to be that in which the gas has a fugacity of 1 atm, while the standard state for the dissolved gas at any temperature is the hypothetical state found by extrapolating the line representing Henry's law on an f_2 versus x_2 graph to unit mole fraction for the dissolved gas.

Assuming ideal gas behavior and validity of the laws for ideal dilute solutions, the thermodynamic functions characteristic of the solution process can now be calculated. Thus

$$\Delta G_2^\circ = RT \ln (H_{2,1} / \text{atm}) \qquad [2.26]$$

$$\Delta H_2^\circ = - T^2 [\, \partial(\Delta G_2^\circ / T) / \partial T \,]_p \qquad [2.27]$$

$$\Delta S_2^\circ = - [\partial(\Delta G_2^\circ) / \partial T \,]_p \qquad [2.28]$$

$$\Delta C_{p2}^\circ = [\partial(\Delta H_2^\circ) / \partial T \,]_p \qquad [2.29]$$

Here ΔG_2°, ΔH_2°, ΔS_2°, and ΔC_{p2}° are the change in the Gibbs energy, enthalpy, entropy, and isobaric heat capacity for the process represented by

gas (at T, P = 1 atm) = dissolved gas, std state

Evaluation of some thermodynamic functions involves a differentiation step, and this imposes some demands on the accuracy of the experimental technique. The Clarke and Glew equation (first three terms) gives

$$\Delta G_2^\circ = R [A_0 T + A_1 + A_2 T \ln (T/K)] \quad [2.30]$$

$$\Delta H_2^\circ = R [A_1 - A_2 T] \quad [2.31]$$

$$\Delta S_2^\circ = - R [A_0 + A_2 + A_2 \ln (T/K)] \quad [2.32]$$

$$\Delta C_{p2}^\circ = - R A_2 \quad [2.33]$$

For the BK equation (when considering only the first three terms) these are

$$\Delta G_2^\circ = R [B_0 T + B_1 + B_2/T] \quad [2.34]$$

$$\Delta H_2^\circ = R [B_1 + 2B_2/T] \quad [2.35]$$

$$\Delta S_2^\circ = R [- B_0 + B_2/T^2] \quad [2.36]$$

$$\Delta C_{p2}^\circ = - 2RB_2/T^2 \quad [2.37]$$

It is noted that Eq. [2.37] states that ΔC_{p2}° varies inversely with the square of the absolute temperature.

CHAPTER 3

REVIEW OF LITERATURE

3.1 Gases in Hexadecane

Solubility and other physico-chemical data for gases in high molecular weight solvents are required for a number of engineering processes, particularly in the petroleum and petrochemical industries. Although this field has been widely investigated by many researchers for a long time, accurate knowledge of gas solubilities in solvents is still needed over a range of temperatures and pressures.

Gas chromatography (61) has been applied increasingly in solubility measurements. First of all, it has been used as an analytical tool to obtain the amount of gas dissolved in a liquid sample. Second, since the basic process in gas-liquid chromatography (GLC) is the equilibration of a volatile solute between a liquid stationary phase of sufficiently low vapor pressure and a carrier gas, which is nearly insoluble in the stationary phase (helium is most commonly used), the chromatographic technique may be used to determine Henry's constant or activity coefficients at infinite dilution. For the determination of $H_{2,1}$ of vapors and very soluble gases ($H_{2,1}$ < 5 MPa), GLC has been shown to be a fast and reasonably accurate technique (62,63). On the other hand, for light gases which are not very soluble in most solvents (and hence elute rapidly), accurate data cannot be obtained by conventional elution GLC

because of the limitations in the evaluation of the retention time of a hypothetical unretained solute or the mathematical dead time (64-68). An important contribution to this topic is due to Lin and Parcher (69), who have extended the range of applicability of elution GLC up to $H_{2,1} \leq 80$ MPa by using a mass spectrometer as the detection system. They measured Henry's constants of 11 light gases such as Ar, Kr, N_2, and O_2 dissolved in n-hexadecane among other solvents at temperatures between 298 and 413 K.

A survey of the literature reveals that inter-laboratory agreement of gas solubilities in various solvents is usually no better than ± 5 %, and direct comparisons of the solubility data by the GLC and static methods are few (70-72).

3.2 Gases in Toluene

The solubilities of methane, carbon dioxide, and sulfur dioxide in toluene are of technological interest because of the occurrence of these gases in natural gas, crude oil, and numerous chemical processes.

Waters *et al.* (73) measured the solubility of propane in toluene at atmospheric pressure and temperatures ranging from 253 to 298 K.

Battino and co-workers (35,74) have reported solubility data for carbon dioxide, nitrogen, and methane in toluene in the temperature range 283 to 313 K. They have compared the thermodynamic functions obtained from their experimental data with the results obtained through application of the scaled

particle theory to gas solubilities.

Kim and co-workers (75) measured vapor-liquid equilibrium data for carbon dioxide in toluene, in benzene, and in p-xylene for pressures up to 6.5 MPa and temperatures from 353 to 393 K.

Lorimer *et al.* (38) have reported total vapor pressures for binary liquid mixtures of chloroform, acetone, toluene, m-xylene, and mesitylene with sulfur dioxide at 228, 237, and 250 K. These authors have interpreted excess functions for all of their systems using association models which involve a self-association constant for sulfur dioxide (component B), a binary association constant, and either a constant describing intermolecular interactions among complexes or a self-association constant for component A.

3.3 Gases In Bitumen

One of the enhanced oil recovery methods is to pump gas (natural gas, carbon dioxide or nitrogen) into the reservoir from an injection well. Some of the gas dissolves in the oil, making it easier to flow and the rest of the gas pushes the oil toward the production well. Therefore, information about the solubilities of gases in bitumen and in oils (both heavy and light) is needed in connection with the actual and potential uses of gases to aid *in-situ* production of bitumen from oil sands and in connection with similar uses of gases in enhanced recovery of heavy and light oils. There is also some interest (related to froth floation etc) in the solubilities of gases in bitumen that is diluted with or dissolved in naphtha or other diluents/solvents.

The bitumens from various areas in Alberta differ widely in their physical and chemical characteristics. Hence no single composition represents all of the oil sands deposits in Alberta. It becomes necessary, therefore, to determine the properties of many samples from various tar-sand deposits.

Because users of gas solubility data need such information for various temperatures and pressures and for many different bitumens and oils, It is impractical to measure every solubility that might be needed. Instead a more general approach is to make maximum use of a "reasonable" number of supposedly reliable solubility data in two ways.

One way is to make use of thermodynamic equations that permit very reliable interpolations and reasonably reliable extrapolations. Another complementary approach is to develop and make use of predictive methods (mostly based on equations of state), which require some experimental data for "test" systems to permit evaluation of reliability of the proposed method and also to permit evaluation of one or more empirical parameters that have always been needed in such treatments. Therefore, the need for suitable correlations for the prediction of solubilities of gases in bitumen cannot be overemphasized. Such correlations will find extensive applications in numerical simulation of the extraction of tar-sands by *in-situ* techniques such as CO_2-injection, fire flooding etc.

Svrcek and Mehrotra (76-78) measured the viscosities, densities and gas-solubilities of bitumen samples from different regions of Alberta, saturated

with CO_2, CO, N_2, CH_4, and C_2H_6 gases. The temperature range of their data is between 285 to 383 K and pressure range to 10 MPa or below. Based on these experimental data, correlations were proposed by these authors (76). Furthermore, Svrcek and Mehrotra (79) have used the Peng-Robinson equation of state to correlate the phase behavior of CO_2- and C_2H_6-bitumen systems at lower temperatures. Lu and co-workers (80) also made use of the Peng-Robinson equation of state to correlate the solubilities of gases in Athabasca bitumen at temperatures other than those already investigated. Moreover, Bishnoi *et al.* (81) presented a computational scheme for the prediction of CO_2 and CH_4 solubilities in bitumen.

CHAPTER 4

EXPERIMENTAL

Many methods of procedure and kinds of apparatus have been used in the measurement of gas solubility. Most of these can be categorized as either chemical or physical. Chemical methods depend on specific chemical properties of the gas, and thus can be used with only a limited number of gases. Physical methods usually depend on no such specific properties and are thus more general. When suitable chemical methods are available, however, they are frequently more accurate and sometimes quicker.

Physical methods may be divided into two broad classifications. First, there are saturation methods in which a previously degassed solvent is saturated with a gas under conditions where appropriate pressure, volume, and temperature may be determined. And secondly, there are extraction methods where the dissolved gas in a previously saturated solution is removed under conditions in which the pressure, volume, and temperature may be determined.

Equilibrium saturation conditions have been attained for the gas and liquid phases by shaking a mixture of the two, by flowing a thin film of liquid through the gas, by bubbling (usually via a fritted disc) the gas through the liquid, or by flowing the gas over the liquid while it is held stationary on some supporting medium (as in gas-liquid partition chromatography).

Determination of the amount of dissolved gas has been carried out by various physical and chemical methods, volumetrically (and with the supporting

use of manometers) and by mass spectrometry. All of these methods and the factors affecting the precision of gas solubility measurements are discussed in reviews (23,40,82) on solubilities of gases in liquids.

The most important factors affecting the precision and accuracy of gas solubility measurements are: purity of materials, temperature measurement and control, pressure measurement and control, attainment of equilibrium and incomplete degassing of the solvent. Although there have been a few notable examples of higher precision reported in the literature, a precision of 1% appears to be adequate for most practical and theoretical applications. This precision of 1% is achieved using the solubility apparatus and the degassing technique employed in this work.

The solubility apparatus used in this work was designed in this laboratory by Hai-ke Yan (visiting scientist from China) and subsequently improved by Zhong-liang Zhang (visiting scientist from China) and Harbinder Singh (graduate student). The solubility apparatus is based on the principle of attaining saturation (saturation method) by flowing a liquid film through the gas.

4.1 Isobaric Equilibrium Solubility Apparatus

A falling film type apparatus (shown in Fig. 4.1) made of glass was used for the measurement of the solubilities of gases in liquids. The solubility is determined from the volume change, at constant pressure, of the gas in contact with the liquid. The design is similar to those of Morrison *et al.* (83) and Hayduk *et al.* (84) with some modifications. Glass stopcocks were replaced by

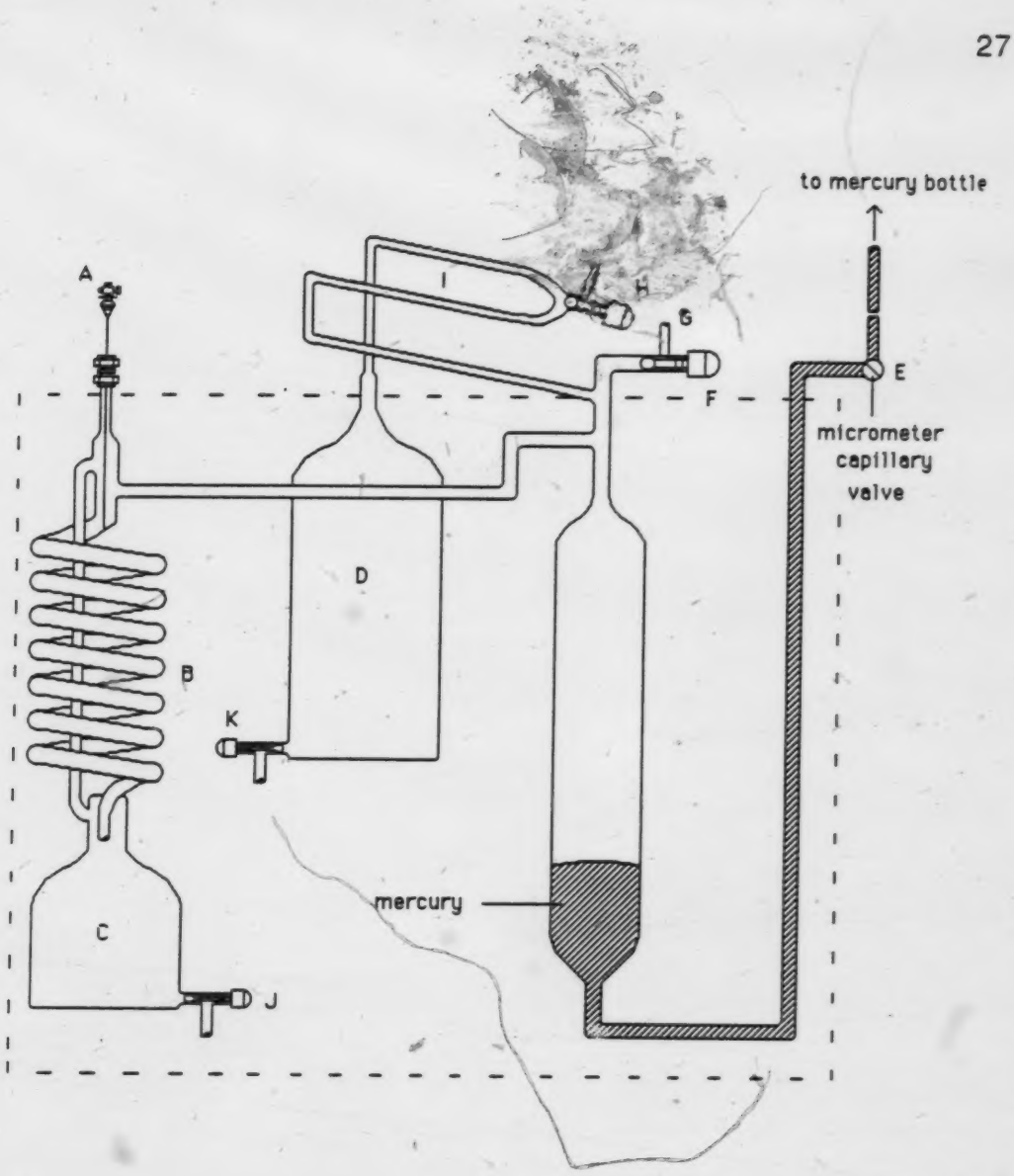

Fig. 4.1. Schematic diagram of the isobaric equilibrium apparatus for determining gas-liquid solubilities : A, Mininert teflon valve; B, spiral; C, receiver; D, buffer; I, U-tube; E, micrometer capillary valve; J, K, H, F, Kontes teflon valves; G, for connection to vacuum assembly/pressure balance apparatus. The dotted line represents a water-filled thermostatted bath.

Kontes high vacuum teflon valves to prevent the contact of vacuum grease with the gas under study, and the interconnection of the system and pressure buffer was achieved with a U-tube. The purpose of the U-tube (which contains the solvent) is to check and control the pressure change in the system. Moreover, the apparatus can be used for temperatures and pressures from 293 to 345 K and to 3 atm.

The apparatus consists of two parts: the system (for dissolution of gas) and the pressure buffer. The system inlets and outlets are fitted with 1/4 inch glass tubing fitted with Swagelok teflon connectors, which make convenient connections to the vacuum system, injection port, and the pressure gauge.

A gas-tight Hamilton syringe mounted on a syringe pump (Model 341 A) has been used for introducing the solvent at low and precise rates. This syringe was attached to a Mininert teflon valve connected to a hypodermic needle. The end of the hypodermic needle touches the wall of the spiral tube to ensure a continuous flow of solvent film.

A known amount of the degassed solvent was continuously injected through the Mininert teflon valve (A). The solvent flows (in a thin film) down the absorption spiral (B) and finally accumulates in the receiver (C). The dimensions of the absorption spiral are about 6 turns of 8 mm glass tubing, 8 cm in diameter. The main premise was that the solvent was saturated with gas at the end of its flow path through this long spiral tube. Upon absorption of the gas, the pressure in the apparatus changes. This pressure change in the system was monitored by means of the solvent U-tube (I) which connects the

pressure buffer (D) to the system. In order to keep the pressure in the system constant, the U-tube was continuously balanced by either adding or by removing (depending on the gas-solvent system) mercury from the system by manipulating the micrometer capillary valve (E).

The Heise pressure gauge (Model 711 B), used for measuring the pressure of the system, can be damaged by some reactive gases that are used. Therefore, for the sulfur dioxide solubility determination it was necessary to isolate the gauge from direct contact with the system. For this purpose we used a mercury-filled U-shaped tube. Details of this glass assembly are shown in Fig. 4.2. A nitrogen cylinder was connected to the gas line. The pressure on the left arm of "U" can be made to balance exactly the pressure on the right arm (the system pressure) by suitable control of nitrogen pressure; hence, this device is referred to as the "pressure balance". Pressure in the left arm of the "U" is adjusted by admission of nitrogen gas, bleeding to the surroundings, or the use of a weak " house " vacuum.

The pressure balance (Fig. 4.2) is connected to the solubility apparatus (Fig. 4.1) at G, via a thick walled teflon tube. At the start of an experimental run valve (L) was closed and valve (N) was opened to the system and the U-tube respectively. The system and filling line are first switched to vacuum until they reach the base pressure (monitored by a Pirani vacuum gauge, Model GP-110, not shown) of the vacuum system. They are then flushed with the gas of interest and finally filled to the working pressure. After allowing sufficient time (4 to 6 hours) for equilibrium, the pressure is measured by balancing the

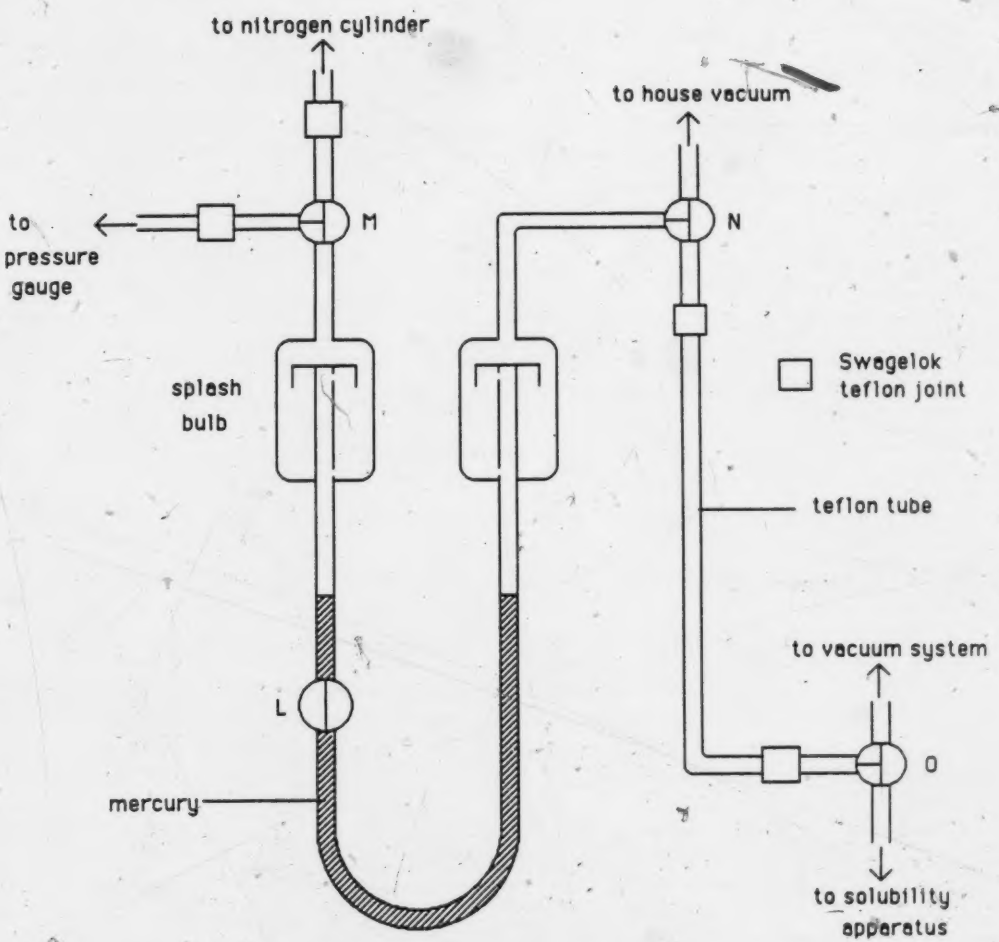

Fig. 4.2. Schematic diagram of pressure balance : M, N, O, three-way teflon valves; L, two-way teflon valve.

mercury U-tube after opening the three-way connection {valve (M)} and valve (L).

4.2 Degassing Apparatus

The degassing apparatus and procedure is similar to that of Battino *et al.* (85) except for the addition of a storage bottle (a) for the degassed solvent (Fig. 4.3). This bottle has a volume of approximately 200 cm^3. Attached to the storage bottle are three-way (b) and two-way (c) teflon valves, and a Kontes high vacuum valve (d) which leads to valve (g) connected to the degassing flask (h). For efficient stirring it was found that a 5 cm long magnetic stirring bar (i) was suitable for splashing the solvent against the walls of the flask.

Approximately 200 cm^3 of solvent was placed in the flask. Vigorous stirring splashes solvent up on the walls of the flask, where it runs down in a film. The basic procedure is as follows. First the cold trap (liquid nitrogen) section is evacuated. Then this section is closed off from the pump (rotary oil pump) and opened briefly (ca 5 sec) to the degassing apparatus. The pressure (Pirani vacuum gauge) is read. The process is repeated until the pressure in the trap section reaches the base pressure of the pump (50 microns). The degassing time was approximately 45 min for water, toluene and n-hexadecane, and 90-120 min for concentrated solutions of bitumen in toluene.

After degassing the solvent, the storage bottle (a) was connected to the degassing flask (h) and was pumped down to the base pressure of the pump.

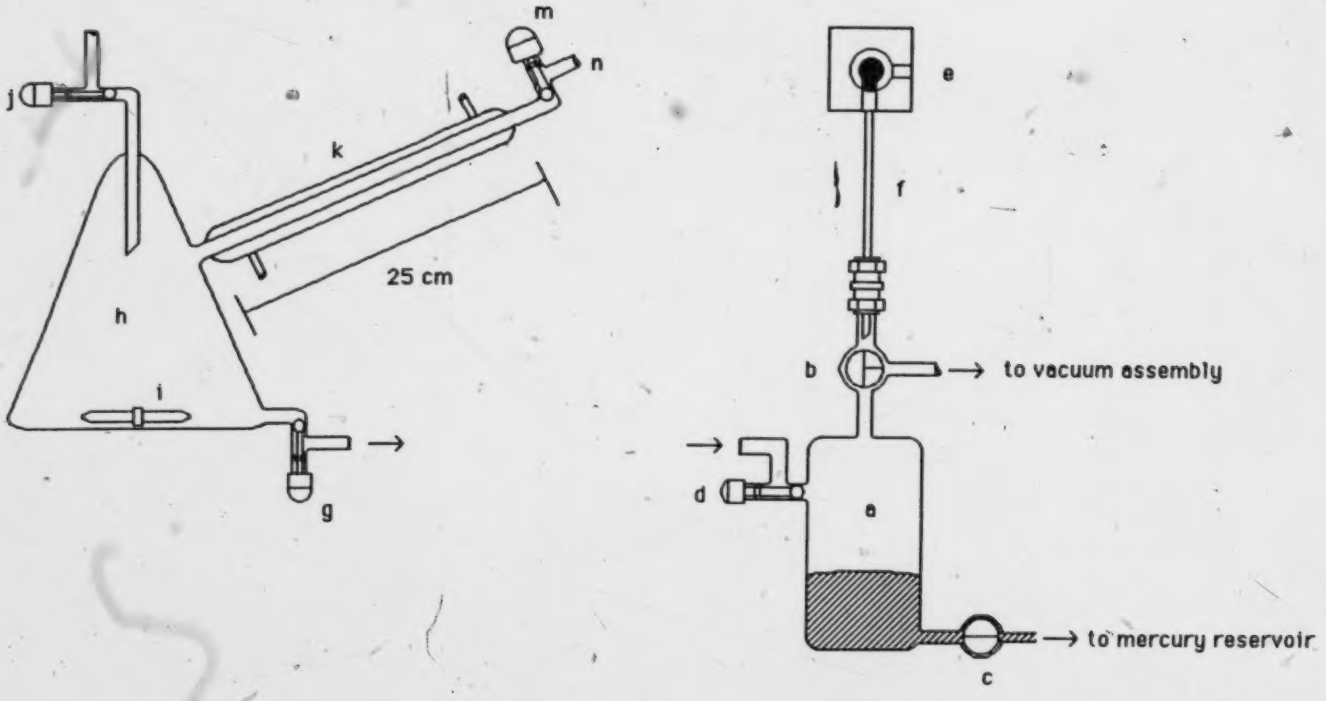

Fig. 4.3. Schematic diagram of the degassing apparatus and the solvent store bottle: h, degassing flask; i, magnetic stirring bar; k, condenser; a, storage bottle; f, hypodermic needle; e, miniature inert valve; d, j, m, g, Kontes teflon valves; c, two-way teflon valve; b, three-way teflon valve; n, for connection to vacuum assembly.

Valve (c) was then opened allowing some mercury to enter the storage bottle which was again pumped down to the base pressure of the pump. The storage bottle was then filled (due to the differential pressure between the solvent flask and the storage bottle) with the degassed solvent by opening the Kontes valves (g) and (d) in that order. The solvent was further cushioned with mercury by opening valve (c). The degassed solvent was withdrawn through the miniature inert valve (e) attached to a hypodermic needle (f). This needle is connected to the storage bottle with a Swagelok teflon union containing a Viton septum.

Although the degassing apparatus and the storage bottle were both made of glass, the connection between the two was with a Teflon tube. It was evident that the solvent used would attack the Teflon tube by extracting the plasticizer. However, after the exposure of a new Teflon tube to a particular solvent for 48 hours, further extraction was negligible.

The dotted line in Fig. 4.1 represents a water-filled thermostated bath. The temperature of the bath was known to ± 0.01°C and was held constant to ± 0.005°C below 40°C and to ± 0.01°C above 40°C, as checked with a platinum resistance thermometer.

The total pressure of the system was measured with a Heise digital-display (Model 711 B) pressure gauge to a precision of 0.02 atm.

4.3 Materials

The gases used for this work were obtained from Matheson Gas Products and Liquid Carbonic Canada, Ltd. All gases were used without further

purification and they had the following specified purities : nitrogen (M.G.P., 99.99 %), carbon dioxide (M.G.P., 99.99 %), methane (M.G.P., 99.97 %), ethane (M.G.P., 99 %), propane (M.G.P., 99.97 %), sulfur dioxide (M.G.P., 99.98 %), and oxygen (L.C.C., 99.5 %).

Toluene (A.R. grade) and n-hexadecane (99 mol %) were obtained from B.D.H. chemicals and were used without further purification. Mercury used was triply-distilled and water was doubly-distilled.

Two kinds of bitumen were used in this work :

1. Bitumen from low grade Athabasca tar sand. Elemental analysis of this bitumen led to the following : 83.44 % C, 10.45 % H, 1.24 % O, 0.48 % N, 4.61 % S, and 0.25 % ash. Several determinations led to values ranging between 540 and 600 g/mol for the average molecular weight of bitumen.
2. Solvent extracted Athabasca bitumen containing 1.1 % toluene was obtained from the Alberta Research Council.

The latter was part of a large sample that was used for some comparative measurements at the Alberta Research Council and the University of Calgary (Svrcek and Mehrotra). This sample of bitumen was described to us as having average molecular weight 560 g/mol and elemental composition as follows : 83.64 % C, 10.24 % H, 1.65 % O, 0.48 % N, and 4.75 % S. Prior to making solutions of bitumen in toluene, the bitumen was dried in an oven at 100°C for two hours under an inert atmosphere of nitrogen.

4.4 Procedure

A brief summary of the experimental procedure follows. A more complete description is included in Appendix A. It is expected that research with the created instrumentation will be continued by future graduate students and these will profit from the detailed descriptions.

At the beginning of the experiment, the apparatus was successively purged and evacuated with solute gas four times through (G). Approximately 2 cm^3 of the solvent was then admitted to the solubility apparatus (Fig. 4.1) through valve (H) to saturate the solute gas with the solvent. The apparatus was finally filled with the solute gas to the working pressure, monitored by the pressure gauge (not shown), which was installed between the vacuum assembly (Fig. 4.4) and the solubility apparatus at (G). Equilibrium was achieved within 4-6 hours. The pressure was measured and some amount of solvent was injected in the U-tube (I) to monitor the pressure change. A known amount of the solvent was then injected through the Mininert teflon valve (A). The gas dissolves in the solvent and causes a pressure change in the solubility apparatus. This pressure change is controlled by manipulating the micrometer capillary valve (E) and so leads to an increase or decrease in the weight of the mercury bottle (not shown). This weight and the amount of the solvent injected were used to determine the mole fraction solubility. A complete solubility measurement at a particular temperature and pressure took approximately 2 to 4 hours.

The attainment of equilibrium was checked by determining the solubility at

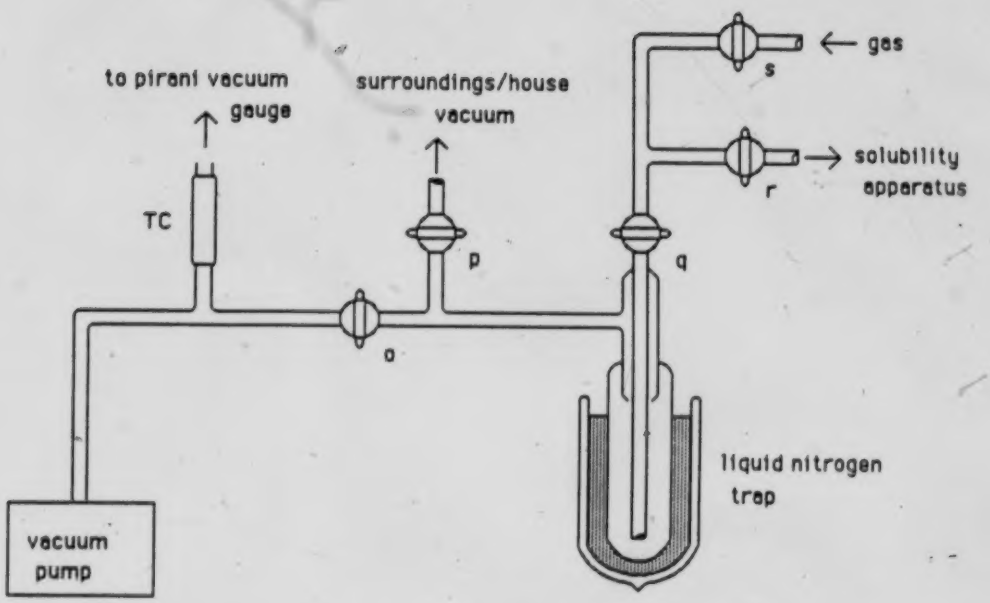

Fig. 4.4. Schematic diagram of the vacuum assembly : TC, thermocouple gauge; o, p, q, r, s, Kontes teflon valves.

different rates of solvent injection. Because the solubilities that were determined from different rates agreed well with those performed at the usual rate, it was assumed that equilibrium was indeed attained.

To assess the performance of the apparatus, we determined the solibilities of oxygen in water at different temperatures and a gas partial pressure of one atmosphere. The results of these measurements and a comparison with the most reliable literature values are given in Table 4.1.

Reproducibilities of our measurements were ± 0.5% except for nitrogen and oxygen solubilities which have an uncertainty of 1%. From Table 4.1, it is clear that the accuracy of the results obtainable with this apparatus is satisfactory, and that the equilibration procedure is adequate.

TABLE 4.1. Comparison of mole fraction solubilities of oxygen in water with literature values at 1 atm partial pressure of the gas and derived thermodynamic functions for O_2 (g) = O_2 (aq).

T (K)	x_2 (10^{-4})	ΔG_2° (kJ mol^{-1})	ΔH_2° / kJ mol^{-1} solubility	calorimetry
298.15	0.2306 [a]	26.47 [a]	-12.13 [a]	-12.00 [d]
	0.2301 [b]	26.48 [b]	-12.11 [b]	-12.06 [e]
	0.2298 [c]	26.48 [c]	-12.06 [c]	-12.03 [f]
308.15	0.1996 [a]	27.73 [a]		
	0.1991 [b]	27.74 [b]		
	0.1988 [c]	27.72 [c]		
318.15	0.1782 [a]	28.93 [a]		
	0.1778 [b]	28.94 [b]		
	0.1779 [c]	28.91 [c]		

[a] This work, [b] Ref. 9, [c] Ref. 25, [d] Ref. 86, [e] Ref. 87, [f] Ref. 88

CHAPTER 5

RESULTS AND DISCUSSION

The solubilities of several gases at several temperatures in hexadecane have been determined using both the equilibrium method and the GLC method. The application of the GLC in the systems studied here is limited to gases having relatively high solubility because of the uncertainty involved in determining the column dead time.

One reason for making these measurements is that hexadecane has been used by previous researchers (69-71,89) as a reasonable model substance for light and largely aliphatic oils. Another reason is that they have provided a very good opportunity to check certain aspects of the applicability, accuracy, and reliability of the GLC method. In this connection it is noted that hexadecane is a somewhat unusual liquid in that its viscosity is low enough that it can be investigated in the isobaric equilibrium apparatus and its vapor pressure is low enough that it can be investigated over the same range of temperatures by the GLC method.

Henry's constants have been compared with the literature values obtained from the static (71,89) and the GLC methods (67,69,70).

We also report in this study the solubility data for nitrogen, methane, propane, carbon dioxide, and sulfur dioxide in toluene in the temperature range 298 to 343 K and pressure range 0.8 to 3.0 atm.

In addition to the above, experimental data are also presented for the

solubilities of CO_2 and CH_4 in bitumen solutions. The bitumen sample was from the Athabasca region in Alberta and is designated as "Athabasca" bitumen. The solubilities of CO_2 and CH_4 in bitumen dissolved in toluene were determined in the temperature range from 298 to 343 K and pressures from 0.9 to 3.0 atm.

5.1 Results

The mole fraction solubilities (x_2) for gases in toluene at different temperatures and pressures are given in Table 5.4. Henry's constants ($H_{2,1}$) for these gases were obtained from a plot of P_2 / x_2 versus x_2 by extrapolating to $x_2 = 0$. Eq. [2.24] or [2.25], truncated to two terms, was fitted to $H_{2,1}$ values. The parameters of the fit so obtained are listed in Table 5.9 and were used to compute the thermodynamic functions (listed in Table 5.5). It is noted here that our data are too limited in the temperature range to distinguish between the ability of Eqs. [2.24] and [2.25] to fit them. Within the accuracy of the data, the enthalpy of solution (ΔH_2°) and the entropy of solution (ΔS_2°) are temperature independent over the temperature range studied.

The solubilities of methane and carbon dioxide in several toluene + bitumen mixtures at several temperatures and pressures are presented in Table 5.6. Solubilities of carbon dioxide in other bitumen mixtures are given in Table 5.7.

The bitumen used in the former case is designated as sample #1 and that in the latter case is sample #2 (refer to section 4.3 for more information on these samples).

Data for gases in bitumen solutions were treated similarly to data for gases in toluene. The constants obtained from Eq. [2.24] or [2.25] are listed in Table 5.10. Henry's constants and the values of ΔG_2°, ΔH_2°, and ΔS_2° are given in Table 5.8.

It is clearly seen that the solubility of carbon dioxide and of methane in toluene + bitumen solutions decreases with increasing temperature although the extent of such reduction is very small for methane.

Henry's constants (obtained from either the isobaric equilibrium apparatus or the GLC) for eight gases and two vapors in hexadecane at various temperatures are given in Table 5.2. Further, Henry's law was used in converting the solubility at a gas partial pressure (P_2) of slightly more or less than atmospheric pressure to that at exactly one atm. The thermodynamic functions, ΔG_2°, ΔH_2°, and ΔS_2° were calculated for

gas (P = 1 atm) = dissolved gas (std state)

from the temperature variation of Henry's constants (for the isobaric equilibrium method) and are listed in Table 5.3. Eq. [2.20] was fitted to the experimental Henry's constant values (from the isobaric equilibrium apparatus) at different temperatures to obtain the constants of the fit. These constants (Table 5.9) were used to interpolate $H_{2,1}$ values at the standard temperatures

(for comparison purposes, see Table 5.2). Plots of ln ($H_{2,1}$/atm) versus 1/T were linear for all the systems studied (Figs. 5.1, 5.2, and 5.3). A comparison is shown with the literature values. In general, data from both experimental methods agree well with each other.

5.2 Discussion

The following is a comparison of the results obtained from the isobaric equilibrium and the GLC methods :

1. For systems where $H_{2,1}$ < 50 atm, both methods are accurate. For slightly soluble gases such as N_2 and CH_4 ($H_{2,1}$ > 100 atm) the equilibrium method yields precise data, whereas the GLC hardly works at all.
2. Since n-pentane and n-hexane are liquids with low vapor pressures at temperatures of these measurements, the determination of solubilities of their vapors in hexadecane is not possible by our equilibrium method. But these liquids have high enough vapor pressure that their vapors can be withdrawn using a syringe and their solubility in hexadecane can be obtained with the GLC method.
3. In the equilibrium apparatus gases like H_2S that react with mercury cannot be employed as mercury is continuously in contact with the solute.

   Although an eluted peak of H_2S in the GLC shows a tail, it was possible to obtain the solubility from the constant retention time. On the other hand,

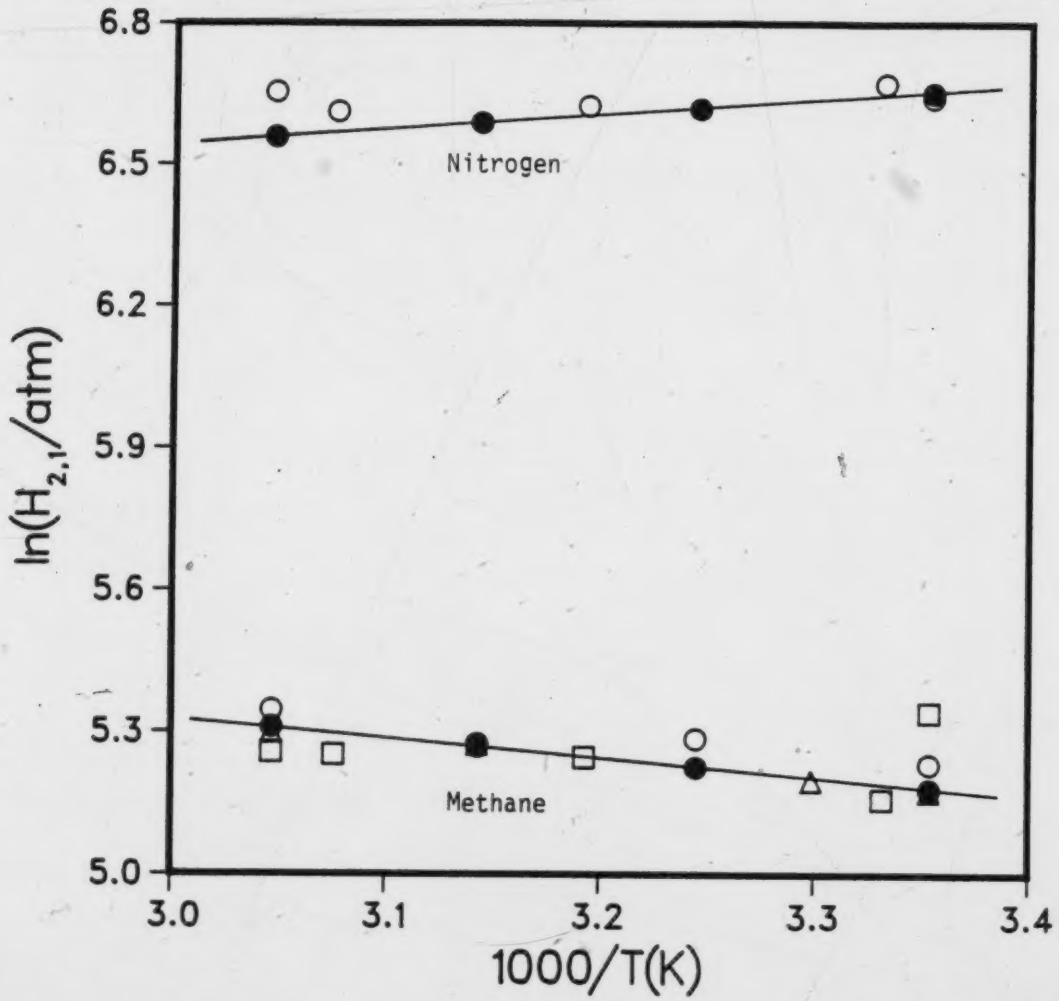

Fig. 5.1. Henry's constants for nitrogen and methane in hexadecane.

Nitrogen: ●, this work; ○, Ref. 69, 89. Methane: ●, this work; ○, GC; △, Ref. 67; □, Ref. 69, 91.

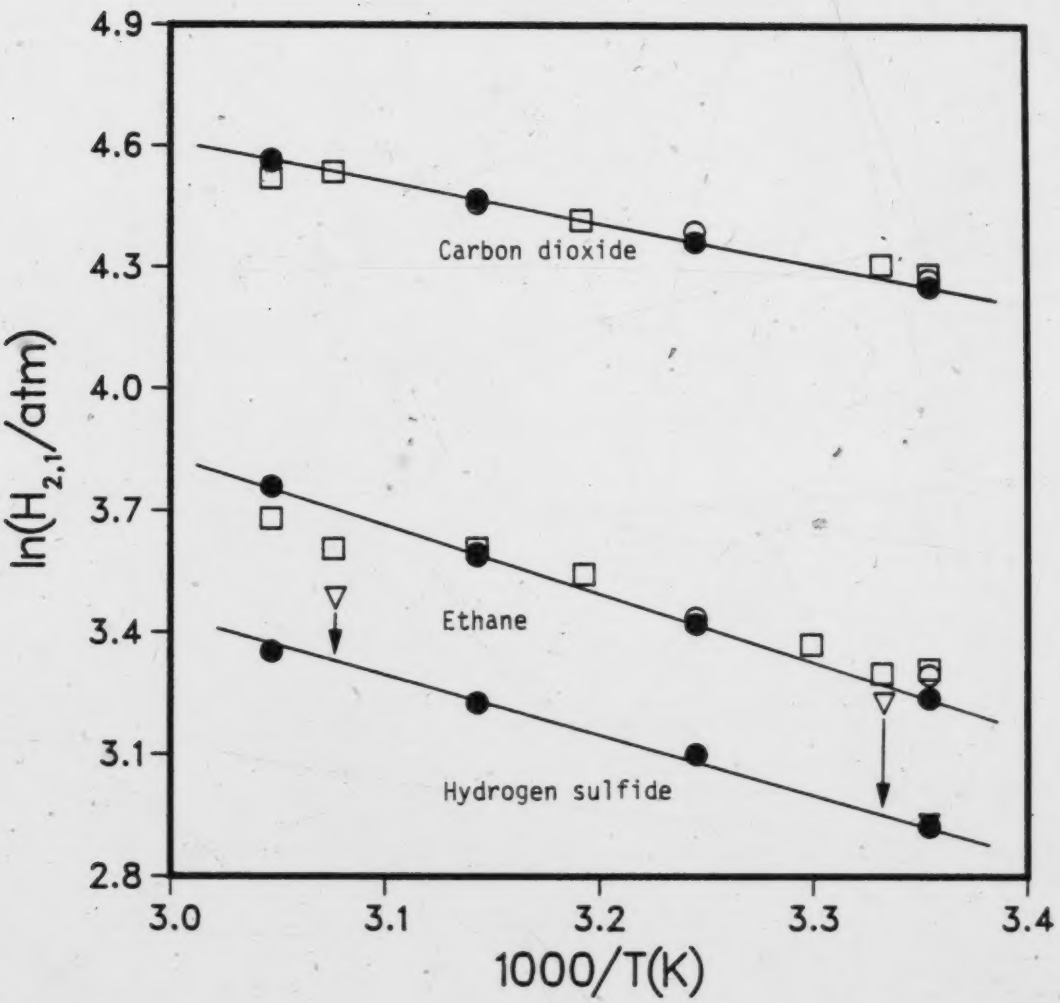

Fig. 5.2. Henry's constants for carbon dioxide, ethane, and hydrogen sulfide in hexadecane. Carbon dioxide: ● , this work; ○ , GC; □ , Ref. 69, 89. Ethane: ● , this work; ○ , GC; □ , Ref. 67, 69, 91. Hydrogen sulfide: ● , GC; ▽ , Ref. 70,89.

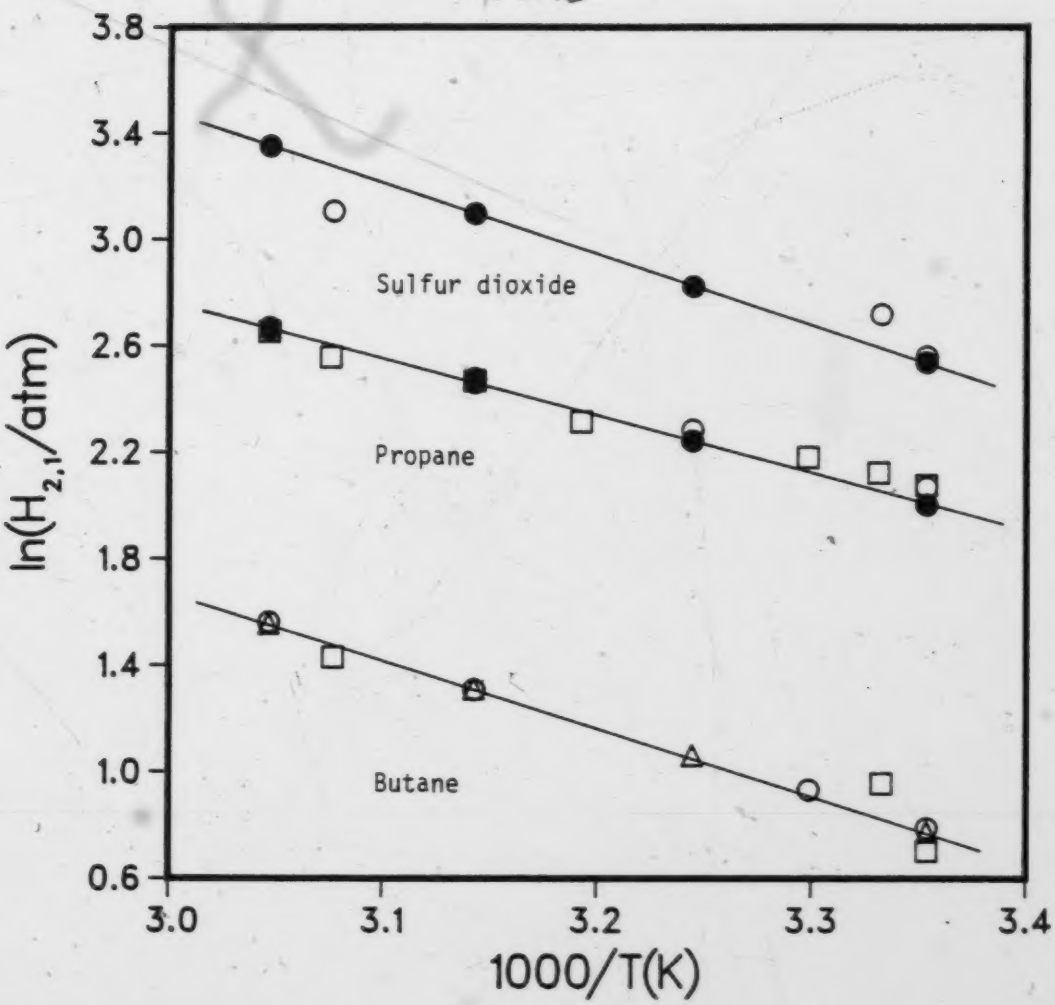

Fig. 5.3. Henry's constants for sulfur dioxide, propane, and butane in hexadecane. Sulfur dioxide: ● , this work; ○ , Ref. 70, 89. Propane: ● , this work; ○ , GC; □ , Ref. 67, 69, 92. Butane: △ , GC; ○ , Ref. 67; □ , Ref. 70, 92.

solubility measurements for SO_2 can be performed in the equilibrium method but not in the GLC because SO_2 reacts with the column material.

4. Measurements using highly viscous solvents cannot be performed by the equilibrium method (as it requires the solvent to flow down the spiral in a thin film) but can be made using the GLC method.
5. Solvents with high vapor pressures are suited only for the equilibrium method as corrections for the solvent vapor pressures are made in the solubility calculations.
6. Although GLC is a fast method for measuring solubilities, the equilibrium method is more accurate when it is applicable.

For results obtained by Choi by the GLC method and reported here, initially the n-alkane series was used to obtain the dead time by applying the method described by Guardino *et al.* (90). It turned out that the t_m values vary slightly with the choice of lower homologous n-alkanes. Secondly, when the retention time of neon gas (67) was used for calculations, the solubilities for some light gases such as methane were lower than literature values. Finally, the dead times were deduced from the solubilities of nitrogen as measured by the equilibrium method (this work) and hence used to evaluate the Henry's constant ($H_{2,1}$) for other solute gases.

Some insight on the effect of temperature on solubility may be obtained by considering the entropy of solution in the Henry's-law limit. Rewriting Eq. [2.28] in terms of mole fraction solubility, we obtain

$$\Delta S_2^{\circ} = - R (d \ln H_{2,1} / d \ln T) = R (d \ln x_2 / d \ln T)$$

where x_2 is the mole fraction solubility when the partial pressure of the gas is 1 atm. The solution of a solute gas into a solvent liquid can be divided into a two-step process: isothermal compression of the gas to a "liquid-like" volume that it occupies when dissolved in the solute, followed by isothermal mixing of the compressed solute with the solvent. The entropy change for this first step is usually negative and dominates at low temperatures while the entropy change for the second step is always positive and increases with decreasing solubility. Thus a point can be reached where the second term dominates and solubility increases with rising temperature.

In non-polar systems, solubilities follow unambiguous trends with the physical properties of the solute and solvent; solubility increases with solute normal boiling point and decreases with solvent solubility parameter (Table 5.12).

In conclusion, the isobaric equilibrium method is first rate for investigating solvents/diluents (such as naphtha, methylene chloride, toluene etc.) and can also be used for investigating light and medium (low viscosity) oils. In addition, this method is also applicable to investigations of bitumens or heavy oils that have been diluted with some other liquid (toluene or naphtha). Finally, it is important to mention that this is a well-established method that is known to yield accurate and reliable results when applied carefully to appropriate low-viscosity systems.

For highly soluble gases, the GLC and the equilibrium methods can be used for measuring the solubilities. However, for systems where $H_{2,1} > 100$ atm, the isobaric equilibrium method is better than the GLC method. It is recognized that an accurate evaluation of the column dead time (for the GLC) is the critical factor for measuring the solubilities of less soluble gases.

The limitation of the isobaric equilibrium method is that it cannot be used with liquids having high viscosities, such as the undiluted bitumens and heavy oils. It is noted here that the GLC method has not been tested on such high-viscosity liquids as bitumens and heavy oils, so there might be an as yet unidentified difficulty specifically attributable to the properties of such substances.

The data presented here may be useful for engineering design and contribute toward the experimental information which will probably lead to a better understanding of the gas solubility. Further work towards understanding of the data and the application of various theories is in progress.

TABLE 5.1: Mole fraction solubilities (x_2) of gases in hexadecane.

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
Nitrogen	298.90	1.233	0.1598
	307.87	1.260	0.1681
	318.65	1.168	0.1608
	330.12	1.078	0.1543
Methane	298.27	1.041	0.5799
	308.17	1.151	0.6258
	312.95	1.140	0.6025
	332.06	1.201	0.5815
Ethane	298.19	1.315	5.035
	307.60	1.240	4.145
	317.84	1.228	3.567
	331.65	1.157	2.892
Propane	298.19	1.043	13.72
	308.00	1.003	10.84
	317.82	0.996	8.998
	329.85	1.088	7.655
Carbon dioxide	298.77	1.090	1.531
	308.16	1.276	1.627
	318.76	1.272	1.473

TABLE 5.1: continued

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
	330.21	1.189	1.201
Sulfur dioxide	298.11	1.103	8.322
	308.16	1.002	6.073
	318.65	1.081	5.317
	335.19	1.047	4.206

TABLE 5.2 : Henry's constants for gases in hexadecane.

Gas	T / K	$H_{2,1}$ / atm	
		Isobaric equil. app.	GLC
Nitrogen	298.15	774.4	
	308.15	748.7	
	318.15	725.3	
	328.15	704.0	
Carbon dioxide	298.15	70.3	71.7
	308.15	78.5	80.6
	318.15	87.2	86.3
	328.15	96.1	95.7
Methane	298.15	177.6	187.4
	308.15	186.0	197.6
	318.15	194.2	195.4
	328.15	202.3	209.8
Ethane	298.15	26.3	27.0
	308.15	30.2	31.1
	318.15	34.3	36.2
	328.15	38.7	

TABLE 5.2 : continued

Gas	T / K	$H_{2,1}$ / atm	
		Isobaric equil. app.	GLC
Propane	298.15	7.5	7.9
	308.15	9.3	9.8
	318.15	11.3	11.9
	328.15	13.6	14.3
n-Butane	298.15		2.17
	308.15		2.89
	318.15		3.71
	328.15		4.74
n-Pentane	298.15		0.65
	308.15		0.91
	318.15		1.24
	328.15		1.67
n-Hexane	298.15		0.20
	308.15		0.30
	318.15		0.43
	328.15		0.61

TABLE 5.2 : continued

Gas	T / K	$H_{2,1}$ / atm	
		Isobaric equil. app.	GLC
Sulfur dioxide	298.15	13.6	
	308.15	16.3	
	318.15	19.4	
	328.15	22.9	
Hydrogen sulfide	298.15		18.6
	308.15		22.2
	318.15		25.2
	328.15		28.6

We have expressed pressures as "standard atmospheres" (1 atm = 0.101325 MPa = 760 mm Hg) and solubilities as mole fractions (dimensionless) so that Henry's constants are expressed in atm. Temperatures (T) are absolute or thermodynamic temperatures, expressed in kelvins.

TABLE 5.3 : Thermodynamic functions for gas (1 atm) = gas (dissolved, std state), for gases in hexadecane for deduced from Eq. [2.24].

Gas	T (K)	$H_{2,1}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
Nitrogen	298.90	771.6	16.52	2.59	-46.6
	307.87	749.4	16.94		
	318.65	726.0	17.45		
	330.12	698.8	17.98		
Methane	298.27	179.5	12.85	-3.53	-54.9
	308.17	183.9	13.39		
	312.95	189.3	13.65		
	332.06	206.5	14.70		
Ethane	298.19	26.12	8.11	-10.45	-62.2
	307.60	30.13	8.69		
	317.84	34.41	9.33		
	331.65	40.01	10.19		
Propane	298.19	7.602	5.01	-16.06	-70.7
	308.00	9.251	5.70		
	317.82	11.07	6.40		
	329.85	14.21	7.25		

TABLE 5.3 : continued

Gas	T (K)	$H_{2,1}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
Carbon dioxide	298.77	71.17	10.58	-8.50	-63.8
	308.16	78.47	11.18		
	318.76	86.37	11.86		
	330.21	99.01	12.59		
Sulfur dioxide	298.11	13.25	6.46	-14.17	-69.2
	308.16	16.51	7.16		
	318.65	20.32	7.88		
	335.19	24.91	9.03		

Table 5.4 : Mole fraction solubility (x_2) results for gases in toluene.

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
Nitrogen	298.15	0.994	0.0528
		2.086	0.1090
		2.678	0.1402
	308.23	1.019	0.0585
		1.835	0.1050
		2.834	0.1600
	323.77	0.935	0.0605
		1.903	0.1209
		2.816	0.1716
	339.59	1.058	0.0758
		1.898	0.1293
		2.722	0.1804
Methane	298.09	0.873	0.2153
		1.898	0.4737
		2.851	0.7156
	308.11	0.982	0.2333
		1.880	0.4522
		2.756	0.6627

TABLE 5.4 : continued

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
	318.65	0.818	0.1891
		1.627	0.3791
		2.849	0.6721
Carbon dioxide	298.09	0.875	0.9065
		1.270	1.335
		2.032	2.149
		2.776	2.925
	307.53	0.856	0.7864
		1.992	1.850
		2.784	2.600
	313.11	0.902	0.7630
		1.891	1.636
		2.632	2.283
		3.020	2.682
	318.90	0.821	0.6615
		1.909	1.546
		2.904	2.378

TABLE 5.4 : continued

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
	327.45	0.866	0.6256
		1.839	1.355
		2.623	1.949
		2.778	2.072
	343.01	1.041	0.6708
		1.881	1.216
		2.446	1.612
Propane	298.11	0.841	5.884
		1.421	9.986
		2.232	16.41
		2.718	20.24
	307.84	1.199	6.681
		1.639	9.388
		2.391	13.81
		2.979	18.16
	318.23	0.694	3.175
		1.081	4.982
		2.003	9.151
		2.759	12.60

TABLE 5.4 : continued

Gas	T / K	P_2 / atm	$x_2 / 10^{-2}$
	323.15	0.724	3.065
		1.218	5.027
		1.958	8.308
		2.776	12.03
Sulfur dioxide	298.11	1.053	26.71
		1.684	41.19
		2.797	62.39
	308.10	0.974	18.55
		1.899	33.54
		2.820	47.02
	318.42	1.013	16.78
		1.957	31.44
		2.586	40.87
	328.03	1.019	13.00
		2.024	23.89
		2.594	29.66

TABLE 5.5 : Thermodynamic functions for gas (1 atm) = gas (dissolved, std state), for gases in toluene deduced from Eq. [2.24].

Gas	T (K)	$H_{2,1}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
Nitrogen	298.15	1868	18.68	7.16	-38.6
	308.23	1722	19.07		
	323.77	1486	19.67		
	339.59	1320	20.28		
Methane	298.09	408.1	14.90	-2.76	-59.2
	308.11	423.0	15.49		
	318.65	438.5	16.12		
Propane	298.11	14.77	6.70	-15.97	-76.0
	307.84	18.75	7.44		
	318.23	21.59	8.22		
	323.15	25.01	8.60		
Carbon dioxide	298.09	96.90	11.35	-9.40	-69.6
	307.53	109.6	12.01		
	313.11	120.2	12.40		
	318.90	124.9	12.80		
	327.45	140.0	13.39		
	343.01	157.8	14.48		

TABLE 5.5 : continued

Gas	T (K)	$H_{2,1}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
Sulfur dioxide	298.15	3.503	3.17	-19.20	-75.0
	308.10	4.811	3.92		
	318.42	5.842	4.69		
	328.03	7.199	5.41		

Table 5.6 : Solubilities of methane and carbon dioxide in toluene + bitumen (sample #1) solutions. See text for definitions of symbols for compositions of solutions and solubilities, and for further description of bitumen.

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	$x_2 / 10^{-2}$
Methane	19.39	298.07	0.861	0.2295
			1.934	0.4968
			2.887	0.7458
		309.29	0.950	0.2294
			1.860	0.4630
			2.925	0.7401
		318.05	0.916	0.2097
			1.904	0.4402
			2.967	0.6931
	37.10	298.08	0.893	0.2465
			1.760	0.4937
			2.957	0.8387
		307.87	0.969	0.2522
			1.928	0.5132
			2.921	0.7961
		318.61	0.920	0.2256
			1.908	0.4806

TABLE 5.6 : continued

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	$x_2 / 10^{-2}$
			2.890	0.7507
	54.25	298.08	0.924	0.2732
			1.870	0.5721
			2.994	0.9932
		308.20	0.957	0.2685
			1.989	0.5832
			2.916	0.8906
		318.46	0.921	0.2446
			1.916	0.5208
			2.870	0.7982
Carbon dioxide	22.06	298.10	0.878	0.9253
			1.819	1.937
			2.826	2.999
		308.27	0.856	0.7836
			1.856	1.723
			2.906	2.698
		318.35	0.818	0.6598
			1.717	1.406
			2.924	2.390

TABLE 5.6 : continued

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	$x_2 / 10^{-2}$
	35.68	298.12	0.852	0.9350
			1.463	1.618
			2.819	3.194
		307.83	0.832	0.8065
			1.963	1.920
			2.772	2.724
		319.24	0.786	0.6607
			1.916	1.627
			2.741	2.342
	43.92	298.36	0.847	0.9486
			1.872	2.095
			2.743	3.098
		307.82	0.829	0.8048
			1.901	1.854
			2.721	2.664
		318.19	0.792	0.6764
			1.931	1.677
			2.734	2.408

Table 5.7 : Solubilities of carbon dioxide in toluene + bitumen (sample #2) solutions. See text for definitions of symbols for compositions of solutions and solubilities, and for further description of the bitumen.

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	x_2 /10^{-2}
Carbon dioxide	23.00	298.15	0.966	1.012
			1.935	2.032
			2.743	2.896
		313.20	0.988	0.8524
			1.914	1.671
			2.769	2.400
		328.20	0.960	0.7063
			1.925	1.437
			2.716	2.030
		343.11	1.033	0.6641
			1.858	1.184
			2.616	1.684
	41.85	298.16	1.015	1.093
			1.954	2.111
			2.719	2.942
		313.24	0.945	0.8387
			1.879	1.696

TABLE 5.7 : continued

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	$x_2 / 10^{-2}$
			2.746	2.471
		328.03	1.016	0.7651
			1.930	1.477
			2.795	2.158
		343.31	1.009	0.6713
			1.901	1.273
			2.565	1.700
	54.24	298.16	0.953	1.046
			1.902	2.087
			2.659	2.930
		313.18	1.024	0.9507
			2.074	1.918
			2.685	2.465
		328.26	0.988	0.7654
			1.938	1.518
			2.639	2.062
		343.13	1.007	0.6948
			1.916	1.305
			2.777	1.897

TABLE 5.7 : continued

Gas	L_w / wt % (Bitumen)	T / K	P_2 / atm	$x_2 / 10^{-2}$
	66.27	298.15	0.989	1.176
			1.728	2.047
			2.854	3.402
		313.16	1.006	1.002
			1.917	1.906
			2.938	2.932
		328.17	0.994	0.8474
			1.978	1.692
			2.968	2.545
		343.15	1.101	0.8144
			1.995	1.505
			2.583	1.963

TABLE 5.8 : Thermodynamic functions for gas (1 atm) = gas (dissolved, std state), for gases in toluene + bitumen solutions deduced from Eq. [2.24].

Gas	L_w / wt % (bitumen)	T (K)	$H_{2,b}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
			Sample #1			
Methane	19.39	298.07	394.6	14.82	-4.34	-64.2
		309.29	421.1	15.54		
		318.05	440.3	16.10		
	37.10	298.08	365.6	14.63	-5.09	-66.2
		307.87	392.1	15.28		
		318.61	417.4	15.99		
	54.25	298.08	353.9	14.54	-3.18	-59.5
		308.20	365.6	15.15		
		318.46	384.2	15.76		
Carbon dioxide	22.06	298.10	95.03	11.29	-10.43	-72.9
		308.27	109.6	12.03		
		318.35	124.2	12.77		
	35.68	298.12	92.40	11.21	-9.73	-70.3
		307.83	103.8	11.89		
		319.24	119.8	12.70		

TABLE 5.8: continued

Gas	L_w / wt % (bitumen)	T (K)	$H_{2,b}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
	43.92	298.36	89.81	11.16	-11.03	-74.4
		307.82	103.4	11.86		
		318.19	118.5	12.64		
			Sample #2			
Carbon dioxide	23.00	298.15	95.88	11.32	-9.27	-69.1
		313.20	115.8	12.36		
		328.20	136.8	13.40		
		343.11	156.2	14.43		
	41.85	298.15	93.09	11.27	-9.07	-68.2
		313.24	113.2	12.30		
		328.03	134.4	13.30		
		343.31	149.6	14.35		
	54.24	298.16	91.33	11.19	-8.89	-67.4
		313.18	107.0	12.20		
		328.26	129.5	13.22		
		343.13	144.4	14.22		

TABLE 5.8 : continued

Gas	L_w / wt % (bitumen)	T (K)	$H_{2,b}$ (atm)	ΔG_2° (kJ mol^{-1})	ΔH_2° (kJ mol^{-1})	ΔS_2° (J K^{-1} mol^{-1})
	66.27	298.15	84.39	10.99	-9.20	-67.7
		313.16	100.5	12.01		
		328.17	117.6	13.02		
		343.15	137.6	14.04		

TABLE 5.9 : Parameters obtained by fitting the equation

$\ln (H_{2,1}/\text{atm}) = A_0 + A_1 / T$ to the data.

Gas	A_0	σ (95%CL)	A_1 / K^{-1}	σ (95%CL)
		Hexadecane		
Nitrogen	5.6090	0.13	311.01	42
Methane	6.6021	0.65	-424.09	204
Ethane	7.4864	0.54	-1257.3	170
Propane	8.4993	0.88	-1931.9	276
Carbon dioxide	7.6801	0.78	-1022.0	246
Sulfur dioxide	8.3239	1.78	-1704.3	560
		Toluene		
Nitrogen	4.6476	0.33	861.47	105
Methane	7.1258	0.10	-332.22	29
Propane	9.1449	2.42	-1920.9	752
Carbon dioxide	8.3719	0.35	-1130.5	112
Sulfur dioxide	9.0229	2.15	-2308.9	672

CL confidence limits

TABLE 5.10 : Parameters obtained by fitting the equation

$\ln (H_{2,b} / atm) = A_0 + A_1 / T$ to the data for toluene + bitumen solutions.

Gas	L_w / wt % (bitumen)	A_0	σ (95%CL)	A_1 / K^{-1}	σ(95%CL)
		Sample #1			
Methane	19.39	7.7278	0.38	-521.48	116
	37.10	7.9564	0.98	-612.04	302
	54.25	7.1534	0.34	-383.03	104
Carbon dioxide	22.06	8.7643	0.98	-1254.6	301
	35.68	8.4509	1.61	-1170.8	495
	43.92	8.9459	0.96	-1326.7	295
		Sample #2			
Carbon dioxide	23.00	8.3075	0.37	-1114.9	118
	41.85	8.2041	0.92	-1090.9	295
	54.24	8.1010	0.79	-1069.8	253
	66.27	8.1448	0.21	-1106.6	66

TABLE 5.11: Partial molar volumes V_2^{∞} (cm^3 mol^{-1}) of various gases at infinite dilution in non polar solvents at 298 K (48).

	Liquid	
Gas	Toluene	Hexadecane
Nitrogen	47.45	50.13
Carbon dioxide	50.52	53.21
Sulfur dioxide	60.90	63.55
Methane	50.50	53.14
Ethane	66.85	69.54
Propane	85.53	88.19

TABLE 5.12 : Pure-component constants [a]

Compound	Mol. wt.	T_b / K	T_c / K	P_c / atm	δ / (cal cm^{-3})$^{1/2}$
Oxygen	32.00	90.0	154.8	50.1	4.00
Nitrogen	28.02	77.3	126.2	33.5	2.58
Methane	16.04	111.7	191.0	45.8	5.45
Ethane	30.07	184.6	305.2	48.2	5.88
Propane	44.09	231.1	369.9	42.0	6.00
Carbon dioxide	44.01	194.7	304.2	72.9	6.00
Sulfur dioxide	64.06	263.2	430.7	77.7	6.00
Toluene	92.13	383.8	594.0	41.6	8.92
Hexadecane	226.44	560.0	717.0	14.0	7.99
Water	18.02	373.2	647.2	218.3	

[a] Values taken from reference 93

TABLE 5.13 : Densities of toluene + bitumen solutions.

L_w / wt% (bitumen)	T/ K	Density (g cm^{-3})
	Bitumen sample #1	
19.39	298.24	0.8880
	308.17	0.8796
	317.23	0.8727
37.10	298.08	0.9119
	307.87	0.9039
	318.61	0.8954
54.25	298.08	0.9370
	308.20	0.9294
	318.46	0.9214
	Bitumen sample #2	
23.00	298.15	0.8939
	313.18	0.8811
	328.18	0.8696
	343.23	0.8559
41.85	298.15	0.9186
	313.24	0.9067
	328.05	0.8981
	343.23	0.8854

TABLE 5.13 : continued

L_w / wt% (bitumen)	T/ K	Density (g cm^{-3})
54.24	298.15	0.9396
	313.16	0.9296
	328.05	0.9194
	343.13	0.9082
66.27	298.15	0.9497
	313.17	0.9388
	328.17	0.9294
	343.15	0.9184

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Appendix A

OPERATING INSTRUCTIONS

Measurement of gas solubilities in liquids using the constant pressure apparatus involves four basic operations: preparing the apparatus to begin an experiment, filling the apparatus with a known quantity of gas, performing an experiment (includes measuring pressure of the system), and cleanup. In addition to these, the procedures for measurements of the pressure of reactive gases, degassing the solvent, and preparation of bitumen solutions are explained. These are now detailed in a step-by-step "drill" which the operator will follow when actually conducting an experiment. Please refer to Figs. 4.1-4.4 for the valve numbering system.

A Preparing the Apparatus

A.1 Initial cleaning

1. Wash the solubility apparatus with the solvent to be used in the experiment and dry using the house vacuum.
2. Close all the valves in the apparatus.
3. Set up the liquid nitrogen trap.
4. Close all the valves of the vacuum assembly.
5. Open the house vacuum line leading to the exhaust of the vacuum pump (not shown in Fig. 4.4).
6. Switch on the vacuum pump and the vacuum gauge.
7. Open valve (o) and evacuate the liquid N_2 trap to about 300 microns.
8. Now open valves (q) and (r) in succession, to evacuate the line running from the pump to the valve (F) of the apparatus. Evacuate to 300 microns.
9. Open valve (F) and pump down to less than 300 microns.

A.2. Filling mercury into the system

10. Fill the mercury bottle with clean mercury.
11. Open valve (E) and slowly allow mercury to enter the solubility apparatus.
    Note: If the Ostwald coefficient of the gas in the solvent is less than 1, fill the mercury reservoir to 4/5 of its volume. This implies that the gas under study is sparingly soluble in the solvent and hence will cause an increase in pressure inside the solubility apparatus, so mercury has to be removed from the apparatus. On the other hand, if the Ostwald coefficient is greater than 1, the mercury reservoir (Fig. 4.1) is filled to 1/3 of its volume (implying that the gas dissolves in the solvent, thus reducing the pressure inside the apparatus). Therefore, mercury is added to the apparatus to compensate for this pressure loss.
12. Once some amount of mercury has been added to the apparatus close valve (E) and continue to pump the solubility apparatus down to below 200 microns. Close valve (F).
13. Cover the valves (J) and (K) with a disposable pipette bulb (in order to prevent contact of water with the valve).

14. Fill the water-bath up to the designated water level and set the temperature controller to the temperature desired.
15. Place the apparatus in the water-bath and wrap the tubing which contains the circulating water from the bath around the U-tube.

B Filling the apparatus with the gas

16. Connect the tubing from the gas cylinder to valve (s).
17. Close valve (r) and open (s), pump down the line leading to the gas cylinder below 300 microns.
18. Now open valve (r) and check if the lines leading to the apparatus and the gas cylinder are below 300 microns (if not wait till the vacuum gauge shows that number).
19. Close valve (q). Using the needle valve of the gas cylinder gauge, introduce the gas into the tubing (leading to the apparatus) up to a pressure of approximately one atm, indicated by a pressure gauge attached between the gas cylinder and the vacuum assembly.
20. Flush out the gas by first closing the needle valve on the gas cylinder gauge and secondly, opening valve (q). Evacuate to less than 300 microns.
21. Close valve (q), and open valve (F) of the apparatus and fill with gas to approximately one atm.
22. Perform operation (19).
23. Repeat steps (19) to (21) three times (i.e. flush the apparatus).
24. Now close valve (F) and very carefully inject 3-4 cm^3 of the degassed solvent through valve (H) (taking care not to let any air bubbles into the apparatus). The solvent is then added to saturate the gas (to be added next). Close valve (H).
25. Close valve (q) and fill the line with gas up to a pressure of 1.5 atm, then open valve (F) and fill with gas up to the desired experimental pressure. **Note:** Always fill the apparatus with gas taking into account the vapor pressure of the solvent at the experimental temperature (i.e. $P_2 + P_{s,1}$).
26. Close valve (F) and open valve (q) and evacuate the vacuum assembly to 300 microns.
27. Close valve (o) and switch off the vacuum pump and the vacuum gauge.
28. Open valve (p) and bleed the vacuum assembly, remove and clean the cooling trap.
29. Leave the apparatus in the water-bath (maintained at a constant temperature) for at least 6 hours, for it to reach equilibrium.

C Performing the experiment

C.1 Measuring the pressure

30. Switch on the Heise pressure gauge (model 711B) 15 minutes before measuring the pressure.
31. Attach the pressure gauge with a Swagelok connector to valve (H), and set the gauge to zero.
32. Open valve (H) and read the pressure from the pressure gauge.

Note: We have to add barometric pressure to this value if measuring the pressure in this manner in order to get P_m.

33. Close valve (H) and disconnect the pressure gauge.
34. Attach a Viton septum to valve (H), and carefully inject some degassed solvent into the U-tubing through this valve, taking care not to allow any air bubbles to enter the system.
35. Wait for the solvent in the U-tube to reach equilibrium (that is when the meniscus level remains stable).
    Caution: Do not allow meniscus levels in the U-tube to drift apart by more than one cm. This can be achieved by either removing Hg (place the Hg bottle lower than the Hg surface inside the system) if the meniscus level in the right limb of the U-tube rises, or by adding Hg (place the Hg bottle higher than Hg surface inside the system) if the meniscus level in the right limb of the U-tube falls, by manipulating valve (E).

C.2 Solubility measurement

36. Fill a gas-tight Hamilton syringe with the degassed solvent.
37. Connect the syringe to the valve (A) and mount it on the syringe pump.
38. Switch on the syringe pump. When the contact between the syringe barrel flange and drive carriage of the syringe pump has been made, open the valve of the syringe and then valve (A).
    Caution: When performing experiments at pressures above one atm, after the above said contact has been made, open the syringe valve and let it be filled with the solvent for about 30-60 sec (depending on the rate of injection) and then open valve (A).
39. Inject about 0.5 ml of the degassed solvent through valve (A) prior to starting the experiment, and control the meniscus level as in step 35.
40. Close valve (A) and then the syringe valve, and then turn off the syringe pump.
41. Weigh the syringe containing the solvent.
42. When the solvent in the U-tube is stable (not moving), make the two menisci levels equal by either adding or removing mercury from valve (E) (this has to be done always prior to weighing the mercury bottle).
43. Weigh the mercury bottle, and then re-attach the mercury bottle.
    Note: Do not let an air bubble enter the mercury tubing. Also, mark the mercury level on the tubing since this must be the same each time the mercury is weighed.
44. Connect the syringe to valve (A) and mount it on the syringe pump. Repeat step 38.
45. Continue injecting solvent, until the desired amount has been injected.
46. Close valve (A), the syringe valve and turn off the pump. Do step 42.
47. Weigh the Hg bottle (see step 43) and syringe again. One run has been completed.
48. To perform further runs, repeat steps 41-47.

D Clean - Up

49. Unwrap the tubing that is around the U-tube.
50. Remove the apparatus from the water-bath.
51. Open valve (H) and (A), and drain out the solution in receiver (C) through valve (J).
52. If the solvent used is a solution of bitumen in toluene, the apparatus must be washed using toluene until completely clean.
53. Close all of the valves except valve (J). Connect the house vacuum tube to this valve and vacuum until system is dry.

E High Pessure Measurements

When performing multiple pressure measurements at one particular temperature (e.g., 3, 2, and 1 atm), it is most convenient to start with the highest pressure and after having completed measurements at that pressure, proceed to the next lower pressure by following steps 54-61.

54. Unwrap the tubing that is around the U-tube.
55. Remove the apparatus from the water-bath .
56. Clean and dry valve (J).
57. Remove the solvent / solution from the receiver through valve (J), leaving behind a small amount surrounding the valve to keep the gas from leaving the apparatus. Close valve (J) and cover it with a pipette bulb.
58. Return the mercury level to its point prior to the experiment either by removing or adding mercury as required.
59. Replace the apparatus in the water-bath and wrap the tubing around the U-tube.
60. Measure the system pressure by performing steps 30-32.
61. With the apparatus open to the pressure gauge, open valve (F) and slowly bleed the apparatus to the desired pressure.
    Note: In order to measure a pressure below 1 atm, the pressure gauge has to be put under vacuum. The following steps give a detailed account of this procedure.
62. A three-way valve (not shown) connects the pressure gauge and the line leading from the vacuum assembly to valve (F) of the apparatus.
    Note: There are two different ports on the pressure gauge to which the tubing from the three-way valve is attached (depending on the nature and the pressure of the gas) : a low pressure clean dry gas port and a high pressure port.
63. Connect the pressure gauge to the three-way valve, which in turn should be connected in between the tubing coming from the valve (r) of the vacuum assembly and valve (F) of the apparatus.
64. Switch on the pressure gauge, and set up the liquid N_2 trap.
65. Close all the valves of the vacuum assembly, switch on the vacuum pump and the vacuum gauge. Now open valves (o), (q) and (r) in that order and also open the three-way valve in such a way that it is open simultaneously to the pressure gauge, to the valve (F) of the apparatus and to the vacuum line.

66. Pump down to about 200 microns, and record the negative pressure on the gauge.
67. Set the three-way valve in such a position that it is isolated from the vacuum assembly, but open to the apparatus.
68. Open valve (F) and read the gauge. Calculate the pressure of the gas in the apparatus. If it is more than the desired pressure, then very carefully open the three-way valve to the vacuum and close immediately. Repeat this until the desired pressure in the apparatus is attained.
69. Let the system stabilize and then record the pressure from the gauge. Close valve (F).
70. Close valve (o) on the assembly line and switch off the vacuum gauge and the pump.
71. Now perform the following. Open valve (p), remove the liquid N_2 trap, disconnect the three-way valve and the pressure gauge.

F Pressure Measurement for Reactive Gases

The Heise pressure gauge, which is used for measuring the pressure of the system, could be damaged by the reactive gases (e.g. sulfur dioxide). Therefore, we used a device called the "Pressure Balance" along with the Heise pressure gauge to measure the pressure of the gas. The pressure balance is connected to the solubility apparatus and the Heise pressure gauge via a teflon tube with Swagelok connectors.

The following procedure gives the details of the pressure measurement using this device, after the apparatus has been filled with the gas and equilibrium has been attained.

72. Make the connections as shown in Fig. 4.2.
73. Close valves (L), (M), (N) of the pressure balance and set the three-way valve (O) to a position so that it is simultaneously open to the vacuum assembly, to the solubility apparatus, and to the pressure balance.
74. Repeat steps 3-8.
75. Open valve (N) to the pressure balance and to the vacuum system (but closed to the house vacuum). Pump down to 200 microns.
76. Set valve (O) so that it is isolated from the vacuum system, but open to the apparatus and to the pressure balance.
77. Switch on the pressure gauge and open valve (F).
78. Position valve (M) so that it is open to the nitrogen cylinder, to the pressure gauge and to the left limb of the pressure balance.
79. Knowing approximately the pressure of the gas in the apparatus, pressurize the left limb of the pressure balance by manipulating the needle valve of the gas cylinder gauge.
80. Slowly and carefully open valve (L) and balance the levels of mercury by either introducing more nitrogen gas or by bleeding the nitrogen to the surroundings.
81. Read the pressure gauge, close valve (F) of the apparatus, and valve (L) of the pressure balance.
82. Bleed the nitrogen gas, hook up the house vacuum tube to valve (N) and

open it to the house vacuum, the pressure balance and to the line leading to the solubility apparatus.

Caution: Do not remove the reactive gases through the vacuum assembly, because : (1) these gases could damage the vacuum gauge, (2) they could react with the vacuum grease of stopcocks (o) and (p), and (3) they tend to contaminate the vacuum pump oil.

83. After about 15 minutes, close off the house vacuum line and disconnect the pressure balance from the pressure gauge, gas cylinder line and the solubility apparatus.
84. Close valve (o), switch off the vacuum pump and the vacuum gauge. Open valve (p), and remove and clean the liquid nitrogen trap.

G Degassing Procedure

A complete step-by-step "drill" falls under two catagories: degassing the solvent and storing the degassed solvent.

G.1 Degassing the solvent

85. Wash the degassing apparatus with the solvent (used for measuring the solubility) and dry it by applying house vacuum.
86. Disconnect the constant pressure apparatus and the gas cylinder tubing at valves (r) and (s), and attach the tubing coming from the valve (m) of the degassing flask and valve (b) of the storage bottle to valves (r) and (s) of the vacuum assembly respectively.
87. Connect a hypodermic needle (f) (attached to the miniature inert valve (e)) to the storage bottle above valve (b) with a Swagelok teflon union containing a viton septum.

    Note: The storage bottle should be clean and dry.
88. Also connect a clean tubing about 8 inches long between valves (g) and (d) of the flask (h), and the storage bottle (a), respectively.
89. Close all the valves on the flask (h) and the storage bottle (a). Open the cooling water to the condenser (k).
90. Set up the liquid nitrogen trap and close all the valves on the vacuum assembly.
91. Switch on the vacuum pump and the vacuum gauge. Then open valve (o) and pump down the liquid N_2 trap to about 200 microns.
92. Now open valves (q), (r), and (m) in that order and evacuate the flask (h) to 200 microns.
93. Attach a teflon tube to valve (j). Close valve (m) and suck in the solvent by dipping the end of the teflon tube in a beaker containing the solvent, while opening valve (j). Now close valve (j).
94. Turn on the magnetic stirrer to a speed such that the solvent is splashed along the inner walls of the flask (h).
95. When the vacuum gauge registers 50 microns, close valve (o) and open valve (m) for a few seconds. Then close valve (m).
96. After waiting for the vapor to freeze out (it takes about one minute), open valve (o) to pump down the liquid nitrogen trap section again to 50

microns or less.

97. Repeat steps 95 and 96 until there is no change (indicated by the vacuum gauge) on opening valve (m) or till the vacuum gauge registers less than 50 microns. Close valve (r).
98. Turn off the magnetic stirrer and close the cooling water tap.

G.2 Storing the degassed solvent

99. When the vacuum assembly is pumped down to 200 microns, open valve (s) and valves (b) and (d) of the storage bottle.
    Note: Valve (b) of the storage bottle is set to a position such that in addition to the vacuum assembly it is also open to the miniature inert valve (e) and to the storage bottle (a).
100. Now open valve (c) and fill in mercury to a level such that it covers this valve. Close valve (c).
101. When the storage bottle is pumped down to 50 microns or the base pressure of the solvent (whichever is lower), open valve (g) and fill the storage bottle with the degassed solvent.
102. Close valves (d) and (g) and set the three-way valve (b) to a position so that it is closed to the vacuum assembly, but open to the miniature inert valve (e) and the storage bottle (a).
103. Place the mercury storage bottle [connected via a polyethylene tubing leading to valve (c)] at a higher level than the miniature inert valve . Slowly open valve (c) to allow mercury to enter the storage bottle (a), and cause the solvent surface in the bottle to rise to the miniature inert valve (e).
    Note: Valve (c) will be left open until all of the degassed solvent has been used.
104. Slowly open valve (e) until one or two drops of the degassed solvent come out. Then close this valve and cap the outlet with a rubber stopper.
105. Close valve (o). Turn off the vacuum pump and the vacuum gauge.
106. Open valve (p). Remove the liquid nitrogen trap and clean it.
107. Remove the connection between valves (d) and (g). Also remove the tubing from valves (r), (s) and attach tubings that lead to the constant pressure apparatus at valve (r) and to the gas cylinder at valve (s).

H Bitumen Solutions

108. Weigh the bitumen needed to make the desired concentration in a beaker.
109. Purge it with nitrogen gas and cover the beaker with aluminum foil.
110. Place the beaker in an oven (maintained at 100°C) for two hours.
111. Remove the beaker from the oven, let it cool to room temperature and dissolve the bitumen in toluene (amount of toluene should be calculated for the proper concentration).
112. Follow steps 85 -107 for degassing and storing the bitumen solution.

H.1 Determination of bitumen concentration

113. Weigh a 100 cm^3 empty round bottom flask with a stopper that has a connection to the house vacuum.
114. Weigh the flask + bitumen solution (obtained by withdrawing 25-40 cm^3 of the degassed bitumen solution through the miniature inert valve (e).
115. Carefully evaporate the toluene from the bitumen solution (could do this by connecting the flask containing this solution to a mild vacuum, i.e. , a house vacuum and heating the contents of this flask with a heat gun, or any other heating device).
116. Weigh the flask + bitumen, and calculate the weight % concentration of bitumen.

Note: To perform experiments with bitumen solutions, 300-400 cm^3 of this solution is degassed and eventually stored in a storage bottle that has a volume of approximately 400 cm^3 (one must anticipate the number of experiments required for each particular concentration and prepare that amount of solution accordingly). It is difficult to prepare the same concentration of bitumen solution twice by this method as the amount of toluene that evaporates and gets trapped in the liquid nitrogen trap during degassing is not the same every time.

H.2 Density measurement of btumen solution

Densities of bitumen solutions {drained out from receiver (C) through valve (J)} were determined for each temperature after the solubility experiment was performed. The glass pycnometers (25 cm^3 nominal volume) were calibrated at each temperature with distilled water. Uncertainties in most of our densities of toluene + bitumen solutions are less than $\pm$ 0.0006 g cm^{-3}. The densities of toluene + bitumen solutions are given in Table 5.13.

Appendix B

DETAILED CALCULATION PROCEDURE

B.1 Temperature

Temperature is measured prior to performing the experiment and during the P-V-T tests using a platinum resistance thermometer (Guildline, Model 95351), precise to ± 0.005°C below 40°C and ± 0.01°C above 40°C.

B.2 Pressure

The total pressure of the system P_m is measured using a Heise pressure gauge. This pressure is a combination of the gas pressure and the solvent vapor pressure

$$P_m = P_2 + P_1 \qquad [B.1]$$

Also the barometric pressure is read , since this value is added to the P_{Heise} (the pressure read from the Heise pressure gauge) i.e $P_m = P_{Heise} + P_{baro}$. Therefore, the pressure of the gas is given by

$$P_2 = P_m - P_1$$

or

$$P_2 = P_m - x_1 P_1^{\circ} = P_m - P_1^{\circ}(1-x_2) \qquad [B.2]$$

where the pure solvent vapor pressure (P_1°) is obtained from the literature (94).

B.3 Mass

The mass of solvent injected and the mass of mercury added in or taken out of the solubility apparatus is corrected for the effects of air buoyancy on the weighings.

Reductions of weighings in Air to Vacuo [from CRC Handbook of Physics and Chemistry (95)].

When the weight w in grams of a body is determined in air, a correction is necessary for the buoyancy of the air. The Table in this book is computed for an air density of 0.0012. The corrected weight is then

$$w^{*} = w + (kw/1000)$$

Values of k are reported in the Tables (CRC Handbook) and are temperature dependent.

B.4 Volume

In an infinitely dilute solution, the partial molar volume of solvent (which we consider to be the material present in excess) is the same as the molar volume of the pure solvent. The partial molar volume of a solute, however, in the same infinitely dilute solution, will generally be different from that of the pure solute, for solute molecules experience a marked change in environment in going from pure solute to an infinitely dilute solution, whereas solvent molecules experience no perceptible change when undergoing the corresponding process. Therefore, the volume of the gas dissolved in the solvent (V) is given by

$$V = (n_1 V_1^{\circ} + n_2 V_2^{\infty}) \pm V_{Hg} \qquad [B.3]$$

where

$$V_{Hg} = w^*_{Hg} / d_{Hg}$$

V_{Hg} is the volume of mercury added to or removed from the solubility apparatus in order to maintain a constant pressure. This mercury is stored in a mercury bottle (Fig. 4.1) and is added or removed from the apparatus by manipulating valve (E) of the solubility apparatus (Fig. 4.1).

Note: Mercury is added to the apparatus when the solubility of gas in liquid is moderate (e.g. for gases such as carbon dioxide, sulfur dioxide, ethane, and propane) and is removed from the apparatus when the solubility is low (for gases such as nitrogen and methane).

d_{Hg} is the density of mercury which is calculated from the following equation obtained from literature (95):

$$d_{Hg}\ (g\ cm^{-3}) = -0.002434\ t\ /°C + 13.5947$$

Similarily, the volume of solvent (V_s) is given by

$$V_s = n_1 V_1^{\circ} = w^*_s / d_s$$

where the density of toluene is obtained from the literature (95) and is given by

$$d_s\ (g\ cm^{-3}) = -0.000943\ t\ /°C + 0.885881$$

For toluene + bitumen solutions, the densities were measured and are given in Table 5.13.

The partial molar volumes (V_2^{∞}) of various gases at infinite dilution in toluene at 298 K were calculated from the semiempirical equation reported by

Handa and Benson (48):

$$V_2^{\infty} P_2^c / R T_2^c = 0.092 + 2.674 T P_2^c / T_2^c P_1^i$$

All the parameters needed to calculate V_2^{∞} were obtained from Reid and Sherwood (93) and are given in Table 5.12. As the internal pressure of the solvent was reported at 298 K, the partial molar volumes computed at this temperature were used for calculating the solubilities at various temperatures and pressures. The internal pressures for toluene (P_1^i = 84.8 cal cm^{-3}) and for water (P_1^i = 41.0 cal cm^{-3}) were obtained from literature (50). The internal pressure can be computed directly from the thermal pressure coefficient or from the coefficients of expansion (α) and isothermal compressibility (β) measured at the appropriate temperatures. At atmospheric pressure (P)

$$P_1^i = (\partial U/\partial V)_T = T(\partial P/\partial T)_V - P \approx T \alpha / \beta$$

Direct measurements of $(\partial P/\partial T)_V$ have been reported for only a few liquids. For hexadecane the P_1^i is computed from separate estimates of α and β. Most of the direct measurements of β have been made at high pressures. Accordingly β was computed at 25°C from isentropic compressibility (β_s) by means of the equation :

$$\beta = \beta_s + (T V_m \alpha^2 / C_p)$$

where β_s = 725.63 T^{-1} Pa^{-1}, V_m = 294.12 cm^3 mol^{-1} (molar volume), $\alpha = 8.83 \times 10^{-4}$ K^{-1} and C_p = 501.45 J K^{-1} mol^{-1} (molar isobaric heat capacity) are taken from Benson and Handa (51). These authors calculated the value of β_s from the observed density (ρ) and ultrasonic speed (u) using the relation :

$$\beta_s = (\rho u^2)^{-1}$$

Note: $V_2^{\infty} = 0$ (as a first approximation) and the approximate value of V is obtained, which is then substituted in the virial equation of state

$$P_2V = n_2RT + n_2BP_2 \qquad [B.4]$$

to compute a new value of n_2. This value of n_2 is now substituted back in Eq. [B.3] to get the correct value of V (now using the calculated value of V_2^{∞}). It is seen that performing this iteration just once is good enough, as further

iterations do not change this value. In the above Eq. [B.4], R is the gas constant, 82.06 cm^3 atm K^{-1} $mole^{-1}$ and B, is the second virial coefficient of the gas obtained from literature (53).

Note : Eq. [B.4] is the virial equation of state written in the pressure-explicit form, neglecting higher powers of P, that is

$$PV / RT = n + nBP + nCP^2 + nDP^3 + \text{------}$$

where B, C, and D are the second, third, and fourth virial coefficients respectively.

By definition the mole fraction solubility of gas in liquid is

$$x_2 = n_2 / (n_1 + n_2) \qquad [B.5]$$

where n_1 and n_2 are the moles of the solvent and the gas, respectively. Therefore, substituting for n_1 and n_2 we have

$$x_2 = \frac{P_2 [(V_s + n_2 V_2^{\infty}) \pm V_{Hg}] / (RT + BP_2)}{(m_1/M_1) + \{P_2 [(V_s + n_2 V_2^{\infty}) \pm V_{Hg}] / (RT + BP_2)\}} \qquad [B.6]$$

As a first approximation, x_2, is set equal to zero and an approximate value of P_2 is obtained from Eq. [B.2], which is then used in Eq. [B.6] to get an approximate value of x_2. This on further substitution in Eq. [B.2] yields a new value of P_2 and hence this new P_2 when applied to Eq. [B.6] yields new x_2. This is carried on until there is no change in the final values of P_2 and x_2. This procedure is refered to as the **Iterative Procedure**.

B.5 Calculation of x_2 for toluene + bitumen solutions

For a three component system the mole fraction equation is written as:

$$1 = x_1 + x_2 + x_3 \qquad [B.7]$$

where the subscripts 1, 2, and 3 denote solvent (toluene), solute (gas) and bitumen, respectively.

As a first approximation, we consider the mole fraction of gas (x_2) to be equal to zero. Therefore, x_1 is calculated directly from the weights

$$x_1 = n_1 / (n_1 + n_3) \qquad [B.8]$$

where the moles of toluene (n_1) is obtained as

$$n_1 = (m_{toluene}) / (M_{toluene})$$
$$= [(m_{solution}) (\text{weight \% of toluene})] / (M_{toluene})$$

and the moles of bitumen (n_3) is computed from the expression :

$$n_3 = [(m_{solution}) (\text{weight \% of bitumen})] / (M_{bitumen})$$

where m represents mass and M represents the molecular weight. The molecular weight of bitumen was taken to be 560 g/mol.

The measured pressure is the sum of the individual pressures of each component

$$P_m = P_1 + P_2 + P_3 \qquad [B.9]$$

The pressure of bitumen (P_3) is taken to be equal to zero. So after rearranging Eq. [B.9] we can write

$$P_2 = P_m - P_1$$
or
$$P_2 = P_m - x_1 P_{s,1} \qquad [B.10]$$

This value of P_2 was used to calculate moles of the gas (n_2).

As a second approximation, x_1 can no longer be calculated directly from the weights due to x_2 being no longer equal to zero. Therefore, one must use the equation

$$x_1 = n_1 / (n_1 + n_2 + n_3) \qquad [B.11]$$

where n_2 was calculated from the first approximation. Therefore, the value of x_1 obtained from Eq. [B.11] was used to calculate a new value of P_2 from Eq. [B.10] and this P_2 was used to obtain a new value for n_2 (using Eq. [B.4]). The final value of x_2 is calculated from the expression :

$$x_2 = n_2 / (n_1 + n_2 + n_3) \qquad [B.12]$$

B.6 Henry's constant ($H_{2,1}$)

Henry's constant was calculated using the following equations :

$$H_{2,1} = P_2 / x_2 \qquad [B.13]$$

$$H_{2,1} = (P_2 / x_2) - (H_a x_2) \qquad [B.14]$$

For gas-liquid systems (oxygen in water and gases in hexadecane) where the partial pressure of the gas was close to one atm and only one pressure measurement was performed at one temperature, Eq. [B.13] was used to compute Henry' constant. On the other hand Eq. [B.14] was used to calculate Henry's constant for gas-liquid systems (gases in toluene and toluene + bitumen mixtures) that deviate from Henry's law at high pressures. Henry's constant in the latter case was obtained from the intercept of the plot of P_2 / x_2 versus x_2.

The Clarke and Glew (54) expression truncated to two terms was fitted to Henry's constant values at different temperatures.

$$\ln (H_{2,1} / \text{atm}) = A + B (T / K)^{-1}$$

The constants (A and B) were further used to compute the thermodynamic properties for the process

$$\text{gas (1 atm)} = \text{gas (dissolved, std state)}$$

Only two terms in the CG equation were considered because for three terms the magnitudes of the errors in the constants were greater than the values of the constants.